

PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Donald R. Huffman

Examiner:

Serial No.: 08/236,933

Art Unit:

Filed: May 2, 1994

Docket: 7913ZAZY

For: NEW FORM OF CARBON

Assistant Commissioner for Patents
Washington, DC 20231DECLARATION OF Harold W. Kroto UNDER 37 C.F.R. §1.132

Sir:

I, Harold W. Kroto, Ph. D., declare and say as follows:

1. I am the Royal Society Research Professor in the School of Chemistry and Molecular Sciences at the University of Sussex, Brighton, United Kingdom. I have attached for the convenience of the United States Patent Office a copy of my curriculum vitae as Exhibit 1, which describes my credentials and demonstrates my expertise in the area of fullerenes.

2. I have reviewed the above-identified application, the Preliminary Amendment therein and the following reference documents, which I understand to be cited in support of a rejection of the present application.

1. an article by K.S. Day, et al., Nature Physical Science 1973, 243, 50-51.

2. an article by Iijima, et al., in J. Phys. Chem. 1987, 91, 3466-3467. ("Iijima et al".).

3. Translation of Russian Patent No. 1,587,000.

4. U.S. Patent No. 2,957,756 to R. Bacon.

5. an article by Kappler, et al., in J. App. Phys., 1979, 50, 308-316.

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3. The application teaches in clear detail to the skilled artisan the preparation of fullerenes, including C_{60} , in quantities that were never recognizably achieved before the discovery by Huffman and Kratschmer described in the application. Specifically, the application describes methods for the production of C_{60} and C_{70} in macroscopic amounts, i.e., amounts that could be seen with the naked eye (inherently at least 10^{18} molecules of product). That discovery for the first time permitted the researchers to confirm the existence and structure of these materials, including subjecting them to general testing of their detailed properties and characteristics, which had theretofore only been projected based upon educated speculation and calculation, grounded upon circumstantial evidence of their existence.

4. I am intimately familiar with the literature concerning and was personally involved in the search for C_{60} and the greater fullerene family: for convenience, one may refer particularly to our review of the literature through 1990 described in an article entitled " C_{60} Buckminsterfullerene, in Chem. Rev. 1991, 1231-1235 attached hereto as Exhibit 2 and for my personal involvement in the research effort in my article entitled " C_{60} : Buckminsterfullerene, the Celestial Sphere that Fell to Earth" in Angewandte Chemie I.E.E. 1992, 31, 111-129, attached as Exhibit 3.

5. I believe it is fair to say that I am among the recognized experts in the subject of fullerenes, and that I was quite cognizant of the state of the art in 1990, and of the early attempted preparation and identification of fullerenes, especially C_{60} and C_{70} .

6. I am familiar with the work of Huffman and Kratschmer on this subject having closely followed their research as described in the Angewandte Chemie article referred to above and attached as Exhibit 3.

7. I am also familiar with the methods described in the above-identified patent application of Huffman and Kratschmer and utilize their principles regularly in producing quantities of C_{60} for research purposes in our laboratories,

8. In my professional opinion the methods for producing the fullerenes, including C_{60} , are described in the application in such manner as to enable one skilled in the art to make and use the same.

9. In my professional opinion, the reference documents listed in paragraph 2 hereinabove, taken individually or collectively, do not teach nor do they claim to teach methods for the production of fullerenes, including C_{60} ; nor is there provided evidence of the production of any such product. Specifically, it cannot be stated that there is any reliable scientific evidence of the formation of C_{60} or C_{70} in any of the references, and no assertion is made that quantities of C_{60} or C_{70} were made. In fact, any such assertion would be entirely speculative and unsupported; to my knowledge, no researcher had proven possession of C_{60} or C_{70} prior to Huffman and Kratschmer.

While Iijima et al alleges that they saw a molecule of C_{60} in the middle of a carbon particle this conclusion is similarly entirely speculative and unsupported by the evidence. Furthermore, Iijima et al did not report in that article a methodology capable of producing and isolating fullerenes in macroscopic amounts.

10. The realization by Huffman and Kratschmer of macroscopic quantities of fullerene and the isolation and characterization of C_{60} and C_{70} by the methods described in the above-identified application is recognized by the knowledgeable scientific community as a long awaited and much needed breakthrough; it was surprising that relatively high yields of fullerene such as C_{60} could be achieved by these methods, as it was expected that no more than $< 1/10000$ parts of target molecules would exist in the soot product and that it would require very sophisticated equipment to isolate quantities of material required to establish and confirm the existence of the products. The difficulties that existed in the quest for C_{60} are well elaborated in the article entitled "Fullerenes" by Robert F. Curl and Richard E. Smalley, printed in Scientific American, Oct. 1991, pp. 54-62 attached hereto as Exhibit 4.

11. Although the discovery described in the Huffman and Kratschmer application may seem simplistic to the uninformed, especially in hindsight, their discovery was quite remarkable. This is readily appreciated if one considers the historical perspective. Ever since the detection of C_{60} by the collaborative efforts of the Smalley and Kroto groups in 1985, as described in the article in Nature, 1985, 318, 162-163, attached hereto as Exhibit 5, experts, such as Drs. Smalley and myself, both together and separately worked to prepare fullerenes on a larger scale. For five long years, many attempts were tried, but each were unsuccessful. Finally, to my knowledge, one group, Huffman and Kratschmer, were the first to find a methodology capable of producing and isolating fullerenes, such as C_{60} , in macroscopic amounts. This methodology is described in their application and satisfied a long felt need in this area.

12. Furthermore, one should not underestimate the significance of their discovery. For the first time, scientists were able to produce and work with samples of fullerenes. They were able to confirm the theoretical predictions about fullerenes and continue to explore new properties of same. Their discovery spawned enormous scientific interest. As a consequence, innumerable investigations and studies relating to fullerenes were conducted, generating more than four thousand publications on the subject. In short, I cannot emphasize enough that their discovery revolutionized the area of fullerenes.

13. I have been requested as well to examine the claims presented by applicants Huffman and Kratschmer. I am not qualified in the law as to the interpretation of claims; but as a scientist knowledgeable in this art, I find the qualifying terms to be aptly descriptive of the methods described and the products produced in the above-identified application, consistently with scientific usage at the time the application was filed.

14. I further assert that the term "macroscopic" aptly and correctly characterizes the breakthrough made by Huffman and Kratschmer in permitting isolation and characterization of the fullerenes C_{60} and C_{70} , in that the term expressly denotes that which can be seen (and therefore tested); that usage is consistently employed in my papers and reviews on the subject entirely independently of Huffman and Kratschmer.

15. In my professional judgement, the above-identified application adequately teaches to the skilled artisan how to make macroscopic amounts of the fullerenes including C_{60} and C_{70} ; furthermore, there is ample evidence in the application that

Huffman and Kratschmer had in their possession macroscopic amounts of these products.

16. I have been among those who sought an appropriate name for this family of often co-produced structurally related material and based upon structure and the historical connection with the geodesic dome structures of Buckminster Fuller, I introduced the name of fullerenes for these molecules in 1987 which was later accepted by the scientific community fullerene by about 1990, and this has become the accepted formal name for these materials, e.g., [60] fullerene and [70] fullerene. I refer in particular to the definition I prepared for McGraw-Hill appearing in McGraw Hill Concise Encyclopedia of Science & Technology, 3rd ed. p. 819 (1994).

17. In summary, I am pleased to lend support to the applications of Huffman and Kratschmer for patent protection; as a researcher in the quest for C_{60} I can keenly appreciate the significance of the defining events reflected in the present application; I can, from my own experience, state with confidence that despite our circumstantial evidence of the existence of these molecules, the inevitable speculation and calculations of properties, and our own convictions, given our knowledge at the time, it was by no means predictable nor obvious to one skilled in the art that fullerenes, such as C_{60} or C_{70} , would be recovered in macroscopic quantities by the methods described by Huffman and Kratschmer in the above-identified application, nor to the best of my knowledge, had such results been claimed.

18. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these

statements and the like so make are punishable by fine or imprisonment or both under section 1001, Title 18 of United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: 9 June 1995

Harold W. Kroto, Ph. D.

CURRICULUM VITAE

Harold Kroto FRS
Royal Society Research Professor

The School of Chemistry and Molecular Sciences,
The University of Sussex, Brighton, BN1 9QJ, UK

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44 273 606755 University main
Fax 44 273 677196 School Fax
elm kroto@sussex.ac.uk

Born 7th Oct 1939 Wisbech, Cambridgeshire, England.

Education

1947-58 Bolton School, Bolton, Lancashire.
1958-61 BSc, University of Sheffield, 1st class honours degree (Chemistry)
1961-64 PhD, University of Sheffield *Electronic Spectroscopy of Unstable Molecules*
Supervisor: R N Dixon FRS (now Professor, Bristol)
1964-65 Postdoctoral Fellow, National Research Council (Ottawa) with D A Ramsay
FRS
1965-66 Postdoctoral Fellow, National Research Council (Ottawa) with C C Costain
1966-67 Member of Technical Staff, Bell Telephone Laboratories, Murray Hill, N.J.
(with Y H Pao, now at Case Western Reserve and D P Santry now at McMaster U)

University Career (University of Sussex 1967-)

1967-68 Tutorial Fellow.
1968-78 Lecturer
1978-85 Reader
1985-91 Professor
1991- Royal Society Research Professor.

Extra-university administration

SRC Millimetre Wave Telescope Sub-Committee 1977-81
SERC Millimetre Wave Telescope Users' Committee 1981-85
SERC Physical Chemistry Subcommittee 1987-90
SERC Synchrotron Radiation Facility Committee 1987-90
SERC Chemistry Committee 1988-91
IAU Sub-group on Astrophysical Chemistry 1987-
MBI Advisory Board of the Max Born Institute (Berlin) 1993-

Meeting (director, organiser or co-organiser)

Brioni International Conferences 1988, 1990, 1993, ...
Royal Society Discussion Meeting 1992
Fullerene Symposium 1993 (Santa Barbara)
Cursos de Verano (El Escorial) *Fullerenos* 1994

Editorial Boards

Chemical Society Reviews 1986- (Chairman 1990-)
Zeitschrift für Physik D (Atoms Molecules and Clusters) 1992-
Carbon (1992-)
J. Chem. Soc. Chem. Comm. (1993-)

Research Details

University of Sheffield

1961-64 PhD in Free radical spectroscopy by flash photolysis

National Research Council

1964-65	Free radical spectroscopy by flash photolysis
1965-66	Microwave Spectroscopy

Bell Telephone Laboratories

1966-67 Raman Spectroscopy of Liquids, Quantum Chemistry

University of Sussex

1967-72	Free radical spectroscopy/flash photolysis
1967-73	Liquid phase interactions/Raman Spectroscopy
1970-	Unstable species/Microwave Spectroscopy
1972-90	Unstable species/Photoelectron Spectroscopy
1976-	Interstellar Molecules/Radioastronomy
1983-90	Unstable species/Fourier Transform IR Spectroscopy
1985-	Cluster Studies/Carbon, Metals
1990-	Fullerene Chemistry, Carbon nanostructures

Temporary Appointments (Visiting Professorships etc)

1974 Visiting Associate Professor, UBC Vancouver (3 months)
 1976 Visiting Scientist, NRC Ottawa (3 wks)
 1978 Visiting Scientist, NRC Ottawa (3 wks)
 1981 Visiting Professor, USC (3 months).
 1983 British Council Visitor, Inst Rudjer Boskovic (Zagreb)
 1987 CNRS (1 month) Univ Paris Sud (Orsay)
 1988- Visiting Professor UCLA (Astronomy)

Extramural Activities

Sport

Tennis and Squash for Sheffield University (1959-1964).
University Athletics Union Finalists - Tennis (1962 and 1963)
President of Athletics Council, Sheffield University (1963-64)

Graphic Art, Design, Television Film

Art Editor Arrows Sheffield University Arts Magazine 1962-64
Winner of *Sunday Times* Book Jacket Design Competition 1963
Editor, design and layout of *Chemistry at Sussex*
 featured in *Modern Publicity* 1979 (international annual of Graphic Design)
Publicity and logos for Chemical Society Meetings
Logo, letterheads for Science and Engineering at Sussex

Publicity, logo, letterheads, poster for BA Meeting 1983
New Scientist BA Advertisement
Logo and letterhead for Inorganic Biochemistry Discussion Group
Logo and letterhead 1990 for *Venture Research International*
(Formerly *BP Venture Research*)
New Cover design and layout for *Chemical Society Reviews*

Chairman of Board of *VEGA SCIENCE TRUST*
Executive producer of five 1-hour Television Films of Royal Institution Discourses for Vega/BBCSelect

Miscellaneous

1981-82	Tilden Lecturer (Royal Society of Chemistry)
1990	Elected Fellow of the Royal Society
1991-	Royal Society Research Professorship
1992	International Prize for New Materials (American Physical Society, R F Curl and R E Smalley)
1992	Italgas Prize for Innovation in Chemistry
1992	Université Libre de Bruxelles (DHC)
1992	University of Stockholm (PhDHC)
1992	Longstaff Medal 1993 (Royal Society of Chemistry)
1992	Academia Europaea (Member)
1993	University of Limburg(DHC)
1994	Hewlett Packard Europhysics Prize (with D R Huffman, W Krätschmer and R E Smalley)
1994	Moët Hennessy*Louis Vuitton <i>Science pour l'Art</i> Prize

RESEARCH

Main research areas:

- I Spectroscopy of Unstable Species and Reaction Intermediates
(Infrared, Photoelectron, Microwave and Mass Spectrometry)
- II Cluster Science
(Carbon and Metal Clusters, Microparticles, Nanofibres)
- III Fullerenes
(Chemistry, Physics and Materials Science)
- IV Astrophysics
(Interstellar Molecules and Circumstellar Dust)

Research Highlights:

- a) Synthesis in 1976 of the first phosphalkenes (compounds containing the free carbon phosphorus double bond) in particular $\text{CH}_2=\text{PH}$ (with N P C Simmons and J F Nixon, Sussex), Refs 1,7.
- b) Synthesis in 1976 of the first analogues of HCP, the phosphalkynes which contain the carbon phosphorus triple bond - in particular CH_3CP (with N P C Simmons and J F Nixon, Sussex), Refs 2,7.
- c) The discovery (1976-8) of the cyanopolyynes, HC_nN ($n=5,7,9$), in interstellar space (with D R M Walton A J Alexander and C Kirby (Sussex) and T Oka, L W Avery, N W Broten and J M MacLeod (NRC Ottawa)), Ref 4-6, based on microwave measurements made at Sussex, Refs 3,7.
- d) The discovery of C_{60} : Buckminsterfullerene in 1985 (with J R Heath, S C O'Brien, R F Curl and R E Smalley), Refs 8,13,15.
- e) The detection of endohedral metallofullerene complexes (with J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, F K Tittel and R E Smalley), Ref 9
- f) The prediction that C_{60} should be produced in combustion processes and might indicate how soot is formed (with Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl and R E Smalley) Ref 10
- g) The explanation of why C_{70} is the second stable fullerene (after C_{60}) and the discovery of the *Pentagon Isolation Rule* as a criterion for fullerene stability in general (Refs 11,13,15)
- h) The prediction of the tetrahedral structure of C_{28} and the possible stability of "tetravalent" derivatives such as C_{28}H_4 Refs 11,15.
- i) The prediction that giant fullerenes have quasi-icosahedral shapes and the detailed structure of concentric shell graphite microparticles (with K G McKay), Refs 12,13.
- j) The mass spectrometric identification and solvent extraction (with J P Hare and A Abdul-Sada) of C_{60} from arc processed carbon in 1990 - independently from and simultaneously with the Heidelberg/Tucson group; Refs 14,15.
- k) The chromatographic separation/purification of C_{60} and C_{70} and ^{13}C NMR measurements which provided unequivocal proof that these species had fullerene cage structures (with J P Hare and R Taylor, Sussex), Refs 14,15.

PUBLICATIONS

180 research papers. One book "Molecular Rotation Spectra" (Wiley 1975) - reprinted with a new preface by Dover 1992.

Main Publications

- 1) M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of unstable molecules by microwave spectroscopy: phospho-alkenes $\text{CF}_2=\text{PH}$, $\text{CH}_2=\text{PCI}$ and $\text{CH}_2=\text{PH}$ ', *J.C.S. Chem. Comm.*, 513-515 (1976).
- 2) M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of the reactive molecule 1-phosphapropyne, CH_3CP , by microwave spectroscopy', *Chem. Phys. Letts.*, **42**, 460-461 (1976).
- 3) A J Alexander, H W Kroto and D R M Walton, 'The microwave spectrum, substitution structure and dipole moment of cyanobutadiyne, HC_5N ', *J. Mol. Spectrosc.*, **62**, 175-180 (1976).
- 4) L W Avery, N W Broten, J M MacLeod, T Oka and H W Kroto, 'Detection of the heavy interstellar molecule cyanodiacetylene', *Astrophys. J.*, **205**, L173-175 (1976).
- 5) H W Kroto, C Kirby, D R M Walton, L W Avery, N W Broten, J M MacLeod and T Oka, 'The Detection of Cyanoheptatriyne, HC_7CN , in Heiles' Cloud 2', *Astrophysics J.*, **219**, L133-L137 (1978).
- 6) N W Broten, T Oka, L W Avery, J M MacLeod and H W Kroto, 'The Detection of HC_9N in Interstellar Space', *Astrophys. J.*, **223**, L105-107 (1978).
- 7) H W Kroto, 'Semistable Molecules in the Laboratory and in Space', Royal Society of Chemistry Tilden Lecture; *Chem. Soc. Revs.*, **11**, 435-491 (1982).
- 8) H W Kroto, J R Heath, S C O'Brien, R F Curl and R E Smalley, ' C_{60} : Buckminsterfullerene', *Nature*, **318**(No.6042), 162-163,(1985)
- 9) J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, H W Kroto, F K Tittel and R E Smalley 'Lanthanum Complexes of Spheroidal Carbon Shells', *J. Am. Chem. Soc.*, **107**, 7779-7780 (1985).
- 10) Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl, H W Kroto and R E Smalley. 'Reactivity of large carbon clusters Spheroidal Carbon Shells and their possible relevance to the formation and morphology of soot', *J. Phys. Chem.*, **90**, 525-528 (1986)
- 11) H W Kroto, 'The Stability of the Fullerenes C_n ($n = 24, 28, 32, 50, 60$ and 70)', *Nature* **329**, 529-531 (1987)
- 12) H W Kroto and K McKay, 'The Formation of Quasi-icosahedral Spiral Shell Carbon Particles' *Nature*, **331**, 328-331 (1988)
- 13) H W Kroto "Space, Stars, C_{60} and Soot", *Science*, **242**, 1139-1145 (1988)
- 14) R Taylor, J P Hare, A K Abdul-Sada, and H W Kroto, "Isolation, Separation and Characterisation of the Fullerenes C_{60} and C_{70} : The Third Form of Carbon." *J. Chem. Soc. Chem. Commun.*, 1423-1425 (1990)
- 15) H W Kroto " C_{60} : Buckminsterfullerene, the Celestial Sphere that Fell to Earth", *Angewandte Chemie* **31**, 111-129 (1992)

SYMPOSIUM LECTURES and SEMINARS

Plenary/Invited Lectures

- 1974 Symp on High Resolution Spectroscopy (Columbus, Ohio)
1976 Symp on Molecular Structure (Austin, Texas)
1978 Faraday Society Spectroscopy Con (Bristol)
1979 14th Internat Free Radical Conf (Sanda, Japan)
Symposium Interstellar Molecules (Meudon, France)
1980 University College Astronomy Symposium (London)
1981 Conference on Submillimetre Wave Astronomy (London)
Advances in Spectroscopy, Faraday Meeting (London).
1983 British Association BAYS lecture (x2) (Sussex)
Federation of Astronomical Socs, Herstmonceux
RAS Disc Meeting on Interstellar Grains (London)
1984 Symposium on Molecular Structure (Austin, Texas)
Microwave/IR Spectrosc of Transients (Cambridge)
EUCHEM Reactive Species in Inorg Chem (Burghausen)
1985 High Resolution Spectroscopy Conference (York)

1986 NATO Workshop PAHs in Space (Les Houches)
Conference on Molecular Astrophysics (Bruxelles)
Symp on Planetary Science, Obs. de Paris (Meudon)
Brioni Conference on Clusters (Brioni, Yugoslavia)

1987 Roy Soc Discussion on The Solar System (London)
High Resolution Spectroscopy Symp (Dijon, France)
Roy Soc of Chemistry Autumn Meeting (Nottingham)
NASA Workshop on Carbon in Space (Ames CA)

1989 Internat Symp on New Aromatic Compounds (Osaka)
Carbon Conference (Pennsylvania State)
ACS Conference (Clusters) Miami
Japan/UK SERC Symposium IMS (Okazaki, Japan)
Faraday Discussion on Clusters (Warwick)
6th ISNA Meeting (Osaka)
Faraday meeting on Clusters (Warwick)
19th Carbon Conference (Pennsylvania State Univ)

1990 German Chem Soc Meeting, Organ Chem (Bad Nauheim)
Solar System Workshop (Clemson, North Carolina)
IOP meeting (Warwick)
Comet Meeting (Bad Honnef Bonn)

1991 4th Chemical Congress of North America (Fuel Science NY)
6th Symposium on Macrocyclic Chemistry (Sheffield)
20th Biennial Conference on Carbon (Santa Barbara)
74th Canadian Chemistry Conference (McMaster, Hamilton)
IOP Annual Meeting, Low Temperature Physics (Birmingham)
Rank Prize Workshop on Molecular Cages (Lake District)
British Association meeting BAYS lecture (Plymouth)
Mackay Symposium (Birkbeck College)
IAU Congress Astrochemistry (Campos de Jordao, Brazil)
Swedish Physical Society (Stockholm)
Fullerene Workshop (RISU, Roskilde, Denmark)
Condensed Matter Physics 1991 (CMMP 91, Birmingham)

1992 Workshop on Atoms and Clusters 92 (Atami, Japan)
Symp. on Atomic and Molecular Structure (Trentino)
Portuguese Chemistry Society Meeting 1992 (Lisbon)

1st Italian Fullerene Conference (Bologna, Italy)
 IOP meeting on Fullerenes (Rutherford Lab)
 Universite Libre de Bruxelles Conference (Belgium)
 Pittcon 92 Conference (New Orleans, USA)
 American Physical Society meeting (Indianapolis)
 Leermaker Symposium (Wesleyan U, Conn, USA)
 Infrared Astronomy Conference (Calgary, Canada)
 Adriatico Conference on Clusters (Trieste, Italy)
 Invited Lecturer Cursos de Verano 92 (El Escorial)
 European Materials Res Soc Meeting (Strasbourg)
 IOP/RSC Joint Symposium on Fullerenes (London)
 Vacuum Ultra Violet Meeting (VUV10, Paris)
 11th Canadian Theoretical Chem. Conf. (Montreal)
 12th Conf on Chemical Education (UCDavis, USA)
 23rd European Conf, Mol Spectros (EUCMOS23, Vienna)
 Symposium fur Theoretische Chemie (Blixen, Italy)
 Gordon Conference on Clusters (Irsee, Germany)
 Italgas Chemistry Prize Lecture (Turin)
 University of Helsinki (Spec Lect) (Finland)
 Gordon Combustion Conf (Spec Lect) (Hawaii)

1993

Italian Fullerene/Superconductivity Meeting - Pisa
 Croatian Chemical Society Symposium - Zagreb
 Fullerene/Superconductivity Meeting - Kirchberg
 ACS Meeting (Fullerenes) - Denver
 Sydney Leach Symposium - Paris
 Theoretical Symposium - Namur
 NATO Fullerene Workshop - Crete
 Centenary Conf of Norwegian Chemical Society - Oslo
 Fullerenes 93 Symposium - Santa Barbara
 IURCAM Conference - Tokyo
 Solid State Devices Conference - Tokyo
 Span/American Inorg Chem Conf - Santiago (Spain)
 Brioni International Conference - Brioni
 Materials Conference - Wroclaw (x2)
 Spanish Materials Conference - Oviedo
 ACOLS Conference - Melbourne (x2)
 London Schools Science Symposium

1994

Association of Science Education Conference (Birmingham)
 New Organic Materials Conference (Madrid)
 Science Research Institute Inaugural Meeting (Salford)
 Student Chemical Society Centenary Meeting (Sheffield)
 Berzelius Dagarna (Stockholm)
 European Physical Society - Hewlett Packard Prize Lecture (Madrid)
 Sussex University Science Teachers Conference (Sussex)
 World Affairs Conference (Boulder, Colorado) (x2)
 Cluster Workshop (Ameland, Netherlands) (x4)
 3rd Workshop on Advances in Phys Chem (Nanjing, China)
 Cursos de Verano Fullerene Workshop (El Escorial, Spain)
 LVMH Science pour l'art Prize lecture (Paris, France)
 Gordon Conference (Ceramic Materials) New Hampshire (special lecture)
 Materials Research Soc Meeting (Boston)

Named/Special Lectureships

1992

Probst Lecture - Southern Illinois Univ (USA)

1993

Cherwell-Simon Lecture (Oxford)
 Steinhofer Lecture (Kaiserslautern)

Dreyfus Lecture (UCLA)
John Coffin Memorial Lecture (University of London)
30th Anniv Lecturer (Chinese Univ of Hong Kong)

- 1994 Brode Lecturer (Whitman College, Washington, USA)
Winegard Lecturer (Guelph University, Ontario, Canada)
Kolthoff Lecturer (University of Minnesota, USA)
Rayleigh Lecturer (Harrow School)
Chemical Inst of Canada Lecturer (Sherbrook University, Quebec, Canada)
Distinguished lecturer (University of Kentucky, Center for Applied Energy Research)
- 1995 Werner Lecturer (Trinity College, Dublin)
Tizard Lecturer (Westminster, School)

Research Seminars (Overseas)

- 1974 Bell Telephone Labs (NJ), NRC (Ottawa), UBC (Vancouver)
1976 Paris Sud (Orsay), Harvard, NRC (Ottawa)
1977 Lille, Brussels, Montreal, Waterloo
1978 Cal. State (L.A.), Cal Tech.(Pasadena), Arizona (Tucson), USC(Los Angeles), Herzberg
Institute (NRC, Ottawa), UC Berkeley
1979 UBC (Vancouver), Montreal
1980 IBM (San Jose), UC Santa Barbara, USC (Los Angeles), Chemical Society Zurich
1981 UC Berkeley
1982 Trinity College (Dublin), NRC. (Ottawa)
1983 Basel, Kiel, Giessen, Inst.Rudger Boskovic (Zagreb)
- 1985 ETH (Zurich), Basel, Inst. R. Boskovic (Zagreb), Rice Univ. (Houston), Texas A&M,
Texas Tech.
- 1986 Harvard, Guelph-Waterloo, Aachen (Tech Hochschule), Chicago
- 1987 USC (Los Angeles), UCLA (Astron), Berkeley, JPL (Pasadena)
- 1988 UCLA(Chem), Stanford, Arizona(Tucson), Arizona State (Tempe), Tech. Hochschul
(Darmstadt), Max Planck Inst (Martinsried)
- 1989 MPI (Munich), UCLA(Chem), Oregon, JPL(Pasadena), Berkeley, NASA (Moffett Field),
Toronto, Montreal, Guelph.
- 1991 California (Los Angeles, UCLA), California (Berkeley), Cal Tech (Pasadena), California
(Santa Barbara, UCSB), Belo Horizonte (Brazil), Recife (Brazil), Erlangen, Freiburg,
Heidelberg, Shell (Amsterdam), NIST (Washington) NRC (Ottawa), Arizona(Tucson)
- 1992 Pisa (Italy), Michigan (Ann Arbor, USA), Chicago (USA), McGill (Montreal, Canada),
Chemical Society of Zurich, Laue Langevin Laboratory (Grenoble), Aarhus (Denmark),
Helsinki (Finland), Niels Bohr Inst(Copenhagen), Stockholm (DHC lecture), Tokyo
(Japan), Shinshu (Nagano, Japan), Kitagawa Industries (Tokyo Japan), Nobeyama Radio
Observatory (Japan), NRC (Ottawa, Canada)
- 1993 Basel Chemical Society, ULB Bruxelles (DHC lecture), Josef Stefan Institute
(Ljubljana), Limburg (DHC lectures), UC San Diego, Crete, NEC Japan, Shinshu,
Shizuoka, Materials Institute (Warsaw), Milan, Berlin Chemical Society
- 1994 2xRSC (Belgium section) lectures (Brussels) (1 British School), Swedish Royal
Academy (Stockholm), Stockholm University (Physics Dept), Herzberg Inst NRC
Ottawa, Braunschweig, Scherring (Berlin), Humboldt Univ Berlin, Bielefeld, KFA
(Julich), Peking U x2 (Beijing), Bell Labs NJ, UNAM Mexico City, UCLA (Astronomy)

1995

UK Research Seminars (* > 1)

Sussex (Chemistry, Physics, Astronomy, Biology*), Cambridge* (Chemistry and Astronomy Depts), Southampton, Oxford, Reading, Nottingham*, Sheffield*, Warwick, Glasgow, Strathclyde, East Anglia, Coleraine, Manchester*, Edinburgh*, Birmingham, U.C. London (Chemistry and Astronomy), Bristol, ICI, Surrey.

UK General Lectures for Students and Public (Chemistry/Astronomy)

Southampton*, Reading*, Sussex*, Exeter*, Bristol*, Bath, Surrey, Essex, Imperial College, University College, Cardiff*, Kent, Swansea, U.C. North Wales, Portsmouth, Leicester*, Loughborough, Thames, Durham, Leeds, Nottingham, Open University, Cambridge, RSC (Sheffield) RSC (Cumberland), Brighton Astron. Soc., Eastbourne Astron. Soc., Croydon Astron. Soc., Alembic Club (Oxford), U.C. Sussex (Astron, Biology) Q.M.C. Sussex Town and Gown, Mid-Kent Astronomy Society, Royal Institution (Friday Evening Discourse), East Midlands RSC.

- 1993 Bath, Cambridge, Imperial College, Birmingham, Warwick Royal Society, Nottingham, Liverpool, Pfizer Company,
1994 Leicester, Aston, Royal Institution (Friday Evening Discourse (#2)), Sussex, East Anglia, Surrey
1995 Durham, Liverpool, Queen's (Belfast), Coleraine

Schools' Lectures

Christ's Hospital School, Worthing Sixth Form College, Kingston Polytechnic (Schools Lecture), RSC Schools L RSC Essex Schools Lecture, Chelsea College, Charterhouse, London Schools (Q.M.C.), King's School Canterbury, St Dominics 6th form College Harrow, Dreyfus Schools' Lectures, 1986 at Royal Institution, St Paul's School for Girls Open Day Lectures (Sussex), Hurstpierpoint College BAYS Lecture (Southampton)

BROADCAST INTERVIEWS etc

- 1976 BBC Radio (Science Now) "Interstellar Chains"
1977 BBC Radio World Service "Interstellar Chains"
1979 BBC TV OU Film based on my lecture "Chemistry between the Stars"
1985 BBC Radio World Service "Chemistry in Space"
1985 BBC Radio Sussex "Chemistry in Space"
1986 BBC (Science Now) "C60, Buckminsterfullerene"
1989 USA Local Radio Carbon in Space)
1991 BBC Radio programme - "Science Now"
1992 BBC Radio World Service (x2)
1992 BBC TV "Molecules with Sunglasses" Horizon
1992 RAI TV Interview for Italian Television (Premio Italgas)
1992 NDR TV Nord Deutsche Rundfunk Programme on Fullerenes
1993 SFB Radio - Sender Freies Berlin, Radio
1993 UCLA video film Dreyfus Lecture
1994 BBC Select TV - Royal Institution Lecture

RESEARCH GRANTS

- | | | | |
|------|------------------------|-------|--------|
| 1970 | Microwave Spectroscopy | (SRC) | 10 000 |
| 1974 | Microwave Spectroscopy | (SRC) | 24 000 |

1974	Microwave Spectroscopy	(Sch)	10,000
1978	Photoelectron Spectroscopy (with M F Lappert)	(SRC)	18,000
1979	Computer	(SRC)	20,000
1977	PDF (with J F Nixon)	(SRC)	18,000
1977	Astronomy (with T Oka)	(NATO)	2,500
1981	Infra Red Spectroscopy	(SERC)	72,000
1980	Quad Mass Spectrometer	(RS)	5,000
1983	IR spectroscopy	(SERC)	20,000
1986	Jet Cooled i.r.spectroscopy	(SERC)	33,000
1987	Clusters (with A J Stace)	(SERC)	157,000
1992	Fullerene Chemistry with R Taylor/ D R M Walton	(BP/ICI/SERC)	200,000
1992	Cluster Rolling Grant with A J Stace/J N Murrell	(SERC)	300,000

MAIN RESEARCH COLLABORATION

The value of microwave and photoelectron techniques to a wide area of chemistry has been highlighted by fruitful collaboration with colleagues here at Sussex. One important research project carried out with D R M Walton involved the synthesis and study of long chain polyynes. This work led to our detection this species in interstellar space by Radioastronomy carried out with T Oka and astronomers at the Herzberg Institute for Astrophysics, NRCC Ottawa. A project, carried out with J F Nixon has opened up a new field of organophosphorus chemistry. Work has been carried out in collaboration with J P Maier (Basle) to study the ions of unstable molecules is now in progress. Cluster Beam studies on Carbon with R F Curl and R E Smalley (Rice). Astronomy Research has been carried out with M Jura at UCLA. The present Sussex Programme on Fullerene Chemistry is being carried out in collaboration with R Taylor and D R M Walton.

ASSOCIATED RESEARCH PERSONNEL

35 D.Phil students,
10 Chemistry by Thesis students
12 Postdoctoral Fellows.

POPULAR PRESS COVERAGE

Interstellar Molecule Discoveries,

Ottawa Citizen, The Times, The New York Times, New Scientist, Scientific American

Unstable Phosphorus Molecules:

New Scientist

Fullerenes

New York Times (x2), The Daily Telegraph, Houston Chronicle, New Scientist, C&E News, Omni, Sky and Telescope, Science Now, Economist, Der Spiegel, Time, Daily Telegraph.....

TEACHING EXPERIENCE

Lecture Courses (Sheffield University)

(1961-1963) taught O-level Chemistry at Sheffield Technical College

Lecture Courses (University of Sussex 1968-)

Chemistry Highlights Lectures for Freshers
1st and 2nd year Spectroscopy courses
Structural Methods (2nd year course)
Symmetry (2nd year)
Advanced Structure (3rd year course)
Valence Theory for Biochemists (2nd year course).
Rotational Spectroscopy (3rd year option)
Astrophysical Chemistry (3rd year option)
Topics in Chemical Physics (3rd year course)
High resolution Techniques (graduate course)

Lecture Courses (Univ. of Southern California, Los Angeles, 1981)

Chemistry & Spectroscopy of Interstellar Molecules

Seminars and Tutorials (Sussex)

Atomic and Molecular Structure (1st year course).
Mechanistic Principles (1st and 2nd year courses).
Thermodynamics (1 year course).
Conceptual Models (3rd year option course).
Synthesis (1st year course).
Statistical Mechanics

Practical Courses (Sussex)

1st year Introductory Practical Chemistry
2nd year Physical Chemistry (organiser 1978-80)
3rd year Chemistry and Chemical Physics Projects.

ADMINISTRATIVE POSITIONS

University of Sussex

Chairman of the University Safety Committee (1986-7)
School Undergraduate Admissions Organiser (1973-1976).
Chemistry by Thesis Sub-Board (1975-1978), Sec (1976-78).
Chemical Physics Subject Group, Secretary (1974-76), Chairman (1976-82 85-87).
Chemical Physics Sub-Board, Secretary (1974-76) Chairman (1979-83, 85-87)
School Joint Committee (1973-74, 77), Chairman (1974)
White House Careers Weekend (Weekend Residential Seminar Course on Careers for 3rd year students), Organiser (1974)
Editing, design and layout of "Chemistry at Sussex" School, Teaching and Research Handbook (copy available). The cover design was reproduced in "Modern Publicity", a major international annual of the best in graphic art and design
School Chemical Society Lecture Organiser (1987-)
University Senate (1979-1980).
Science Committee (1980, 1981-2, 1985-7)
Laboratory Director (1983-86): Overall responsibility for Tech Staff logistics, deployment, grading etc; School research strategy, budgeting, expenditure, building and laboratory space allocation.

C₆₀: Buckminsterfullerene

E.2

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I. Introduction

In 1967 Palmer and Shelef wrote the definitive review of the early work on carbon clusters in their article on the composition of carbon vapor.¹ Major advances have however been made in the interim period, and the overall situation has been updated by Weltner and Van Zee² who have given a very complete picture of the state of this fascinating field. Although Weltner and Van Zee's review is comprehensive (up to Nov 1, 1988), covering all aspects of carbon cluster properties, recent advances in the story of C₆₀ buckminsterfullerene (Figure 1) indicate that a specialized review is necessary and timely. The existence of the fullerenes as a family has now been established and it is useful to use a convenient nomenclature such as fullerene-60 or fullerene-70 which can apply to the whole family. There are of course numerous possible C₆₀ and C₇₀ cage isomers, however here we shall, in general, mean the most geodesically stable cages for which there is now no doubt in the case of the 60 and 70 atom species—they are (I_h)fullerene-60 and (D_{5h})fullerene-70 where standard symmetry labels have been added as prefixes. Since the existence of fullerene-60 and its spontaneous creation have ramifications in numerous areas from the properties of carbonaceous solids and microparticles through combustion, thermolysis, and synthetic organic chemistry to the nature of the carbonaceous constituents of space, these implications are also surveyed.

During a series of experiments in 1985 which probed the nature and chemical reactivity of the species produced during the nucleation of a carbon plasma the C₆₀ species was discovered to be stable by Kroto, Heath, O'Brien, Curl, and Smalley.³ It was proposed that this



Harry Kroto (left) was educated at Sheffield University and after periods at the National Research Council, Canada (1964–1966), and Bell Telephone Laboratories (1966–1967) went to the University of Sussex where he is now Professor of Chemistry. His research into the production and spectroscopic characterization of new species such as the phosphalkenes, phosphalkynes, thiocarbonyls, and polyynes led, via radioastronomy studies of interstellar molecules, to carbon cluster beam experiments aimed at understanding stellar chemistry. Wahab Allaf (right) who was educated at Aleppo University (Syria) and Sussex University is carrying out research on carbon clusters and laser chemistry. Simon Balm (center) who is studying cluster beam reactions and astrophysical chemistry was educated at Durham University and Sussex University.

stability was due to geodesic and electronic properties inherent in the truncated icosahedral cage structure shown in Figure 1 and the molecule was named buckminsterfullerene. This novel proposal did not receive instant universal acceptance since it appeared to have been based on highly circumstantial evidence. Indeed it is now clear that there was a significant degree of scepticism in the minds of some with regard to the validity of the proposal, perhaps because the evidence was dispersed among many disparate scientific observations, much like the way that C₆₀ itself may—we now realize—be involved in many processes involving carbon in the environment and space. However, systems giving rise to C₆₀ were subjected to many detailed investigations subsequent to the discovery paper,³ and some important points evolved which are worthy of highlighting:

(i) A wealth of convincing experimental evidence was amassed that showed that C₆₀ possessed unique physicochemical stability—a conclusion totally independent of the cage structure proposal.

(ii) The fullerene cage proposal was the simplest and most elegant explanation of the unique behavior and no serious alternative explanation was ever presented.

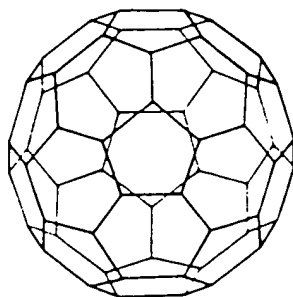


Figure 1. C_{60} buckminsterfullerene.¹

(iii) The proposal was consistent with many earlier observations on bulk carbon and clarified some previously unexplained phenomena in carbon chemistry.

The fullerene structural proposal has recently been confirmed by complementary observations from two groups. Krätschmer, Lamb, Fostiropoulos, and Huffman,⁴ in following up their earlier IR investigation (in 1989)⁵ which suggested that C_{60} might be present in arc-processed graphite, extracted a soluble material which formed crystals. The X-ray analysis showed the material to consist of 10-Å diameter spheroidal molecules and supplementary mass spectrometric and infrared data provided the first unequivocal evidence for C_{60} (and C_{70}). In a parallel, independent investigation which probed this same original key observation,⁵ Taylor, Hare, Abdul-Sada, and Kroto⁶ found that similarly arc-processed graphite gave rise to a 720 mass peak, commensurate with the presence of fullerene-60, and that this material was soluble and could be extracted directly. The extracted C_{60} compound yielded a single ^{13}C NMR line which proved that all 60 carbon atoms are equivalent as expected for the truncated icosahedral buckminsterfullerene structure. Taylor et al. also showed that C_{60} and C_{70} can be separated chromatographically and that the latter has the D_{5h} prolate, ellipsoidal structure first suggested by Heath et al.⁶ These results provide further support for the conjecture that a whole family of fullerenes exists.^{7,8}

Since these revelations, which are discussed further in section IX, the fullerene field has exploded and numerous groups are probing various facets of physicochemical properties of the fullerenes. Indeed a new field of carbon chemistry has been born, and the first faltering steps of the promising infant are described in section X. Thus this review is particularly timely as it is written at the precise moment when the final sentence in the last paragraph of the first chapter in the story of the fullerenes has been completed. The opening paragraphs in the next chapter are just being written and they herald a new era in which the flat world of polycyclic aromatic chemistry has been replaced by a postbuckminsterfullerene one in which round structures are favored under certain surprisingly common circumstances.¹⁰ This article reviews the buckminsterfullerene story from the time when it was just a twinkle in the eyes of a few imaginative theoreticians, through the experiments which revealed that it actually formed spontaneously and exhibited stability to the most recent revelations that it could be isolated and did indeed possess the round hollow cage structure as

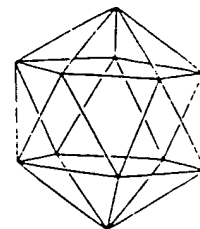
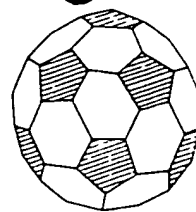


Figure 2. Diagram of C_{60} next to an icosahedron published in the book *Aromaticity* by Yoshida and Osawa.¹⁴ These authors discuss (in Japanese) the "superaromaticity" which might accompany electron delocalization over a three dimensional truncated icosahedral pure carbon molecule.

proposed. As many contributions to the story as could be traced by Dec 1990 are included.

II. Summary of Relevant Carbon Studies Prior to the Discovery of C_{60} Stability

At least part of the reason for the degree of interest engendered by the buckminsterfullerene proposal revolves around its high degree of symmetry. Mankind has always been fascinated by symmetric objects, indeed stone artifacts with the form of the Platonic solids, dating back to neolithic times, have been found in Scotland,¹¹ indicating that human beings have long had a spiritual affinity with abstract symmetry and an aesthetic fascination for symmetric objects. The truncated icosahedron is one of the Archimedean semiregular solids; however in hollow form an early example appears in the book *De Divina Proportione* by Fra Luca Pacioli. A reproduction of this drawing by Leonardo Da Vinci entitled "VCOSEDON ABSCISVS VACVVS" is to be found in the book *The Unknown Leonardo*,¹² which is rather more accessible than the original!

The C_{60} molecule itself was first suggested in a most imaginative and prescient paper by Osawa in 1970¹³ and discussed further in a chapter on "Superaromaticity" in a book by Yoshida and Osawa¹⁴ in 1971; the original diagram is depicted in Figure 2. An equally imaginative article, which actually predates this work, was written in 1966 by Jones in which he conjectured on the possibility of making large hollow carbon cages.^{15,16} The next paper was that of Bochvar and Gal'pern in 1973 who also published a Hückel calculation on C_{60} .^{17,18} In 1980 Davidson published a paper which used graph theory to deduce an algebraic solution of the Hückel calculation for fullerene-60.¹⁹ Davidson's orbital energy level diagram, depicted in Figure 3, was determined by using a calculator, and this paper contains an unusually prescient paragraph in the light of recent observations (particularly those in section VII): "Should such structures or higher homologs ever be rationally synthesized or obtained by pyrolytic routes from carbon polymers, they would be the first manifestations of authentic, discrete three-dimensional aromaticity." Haymet's study²⁰ on this molecule coincided very closely with its discovery in 1985.³

On the experimental front there were many very important early papers on carbon clusters and these have already been reviewed.^{1,2} Perhaps the most interesting early carbon cluster papers (and the ones which in fact actually stimulated the discovery experiments) were

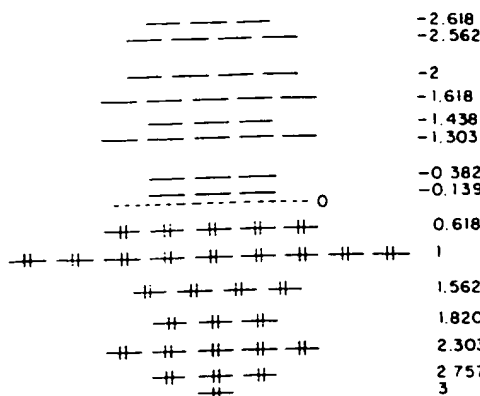


Figure 3. The Hückel molecular orbital calculation for buckminsterfullerene was carried out by Bochvar and Gal'pern^{17,18} (1973) and Davidson¹⁹ (1980), prior to, and by Haymet²⁰ (1985) coincidentally with its discovery. The orbital energy level diagram (units of β) depicted here is that published by Davidson¹⁹ who determined it using graph theory to obtain simplified algebraic relations which were evaluated with a calculator (reprinted from ref 19; copyright 1981 Springer-Verlag Publishers).

those published by Hintenberger and co-workers in 1959–63^{21–24} in which it was shown that species with up to 33 carbon atoms could form in a carbon arc. The next important advance was made by Rohlffing, Cox, and Kaldor²⁵ in 1984 who found that much larger carbon clusters (C_n with $n = 30$ –190) could be produced by vaporization of graphite (Figure 4). Rohlffing et al. used the supersonic nozzle, laser vaporization technique developed by Smalley and co-workers at Rice University²⁶ in 1981. In this technique clusters are made by laser vaporization of refractory materials into a pulse of helium or argon in the throat of a supersonic nozzle. The vaporized material nucleates in the gas pulse which then expands supersonically into a vacuum chamber where it cools and is skimmed. The skimmed beam passes into a second chamber where the entrained clusters are ionized by a second laser pulse and the cluster ion mass distributions determined by time of flight mass spectrometry (TOF-MS). The mass spectrum observed by Rohlffing et al.²⁵ is shown in Figure 4; they pointed out that only ions with *even* numbers of carbon atoms were observable for the new family of clusters with more than 30 carbon atoms. Packing or magic number effects are very weak under these conditions.²⁷ Bloomfield et al.²⁸ also studied carbon clusters by the same technique and observed both positive and negative *even* numbered ions. They also studied the fragmentation behavior of the new family and in particular chose the C_{60} cluster for further study and showed that it could be photodecomposed with 532-nm multiphoton laser radiation.

III. The Discovery of C_{60} : Buckminsterfullerene

In September 1985 the reactions of carbon clusters were investigated by the Rice/Sussex group.^{3,29,30} These experiments were aimed at simulating the conditions under which carbon nucleates in the atmospheres of cool N-type red giant stars. Circumstantial evidence appeared to suggest^{31,32} that such stars might be likely

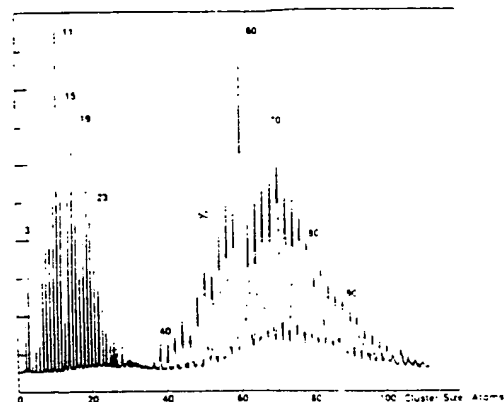


Figure 4. Time-of-flight mass spectrum, observed by Rohlffing, Cox and Kaldor,²⁵ of carbon clusters produced by laser vaporization of graphite. In this experiment carbon clusters with 30–190 atoms were detected for the first time. These studies showed that only even-numbered clusters were stable (reprinted from ref 25; copyright 1984 the American Institute of Physics).

sources of the long carbon chain molecules in the interstellar medium and in particular that the formation process might be related in some important way to soot formation.³¹ The interstellar cyanopolynes (HC_nN ($n = 5$ –11)) were discovered by a synergistic combination of laboratory microwave spectroscopy experiments,^{33,34} theoretical analysis,³⁵ and observational radioastronomy.^{36–39} The cluster beam experiments showed convincingly that species such as HC_nN and HC_nN , which had been detected in space,^{36–38} could be produced by such laboratory simulations of the conditions in carbon stars.^{29,30} A second motivation for probing laser vaporization of graphite was the question of whether carbon clusters were associated with the so-called diffuse interstellar bands as Douglas had proposed in 1977.⁴⁰ The development of resonant 2-photon ionization in conjunction with the cluster beam technique to obtain the high-resolution spectrum of SiC_2 by Michalopoulos et al.⁴¹ suggested that the electronic spectra of carbon clusters might be accessible by this technique. During the course of the experiments^{29,30} which probed the behavior of the pure carbon clusters a striking discovery was made—under some clustering conditions the 720 mass peak appeared to be extremely strong (Figure 5).³ Indeed the intensity of the C_{60} peak, relative to the adjacent cluster distribution, could be varied dramatically just by altering the conditions. In particular, conditions could be found for which the mass spectrum was totally dominated by the C_{60} peak—at least in the mass range accessible (Figure 6). It was concluded that C_{60} must be particularly stable to further nucleation and it was proposed that this might be explained by the geodesic factors inherent in a truncated icosahedral cage structure in which all the atoms were connected by sp^2 bonds and the remaining 60 π electrons distributed in such a way that aromatic character appeared highly likely.³

In these experiments it was found that the C_{70} peak also showed clear enhancement although to a lesser extent; the C_{60}/C_{70} ratio was ca. 5/1 in general. In previous experiments^{25,27,28} the $C_{60}/(C_{58} \text{ or } C_{62})$ ratio was ca. 2/1 (Figure 4) whereas in the new experiments

1) Used 4h
4) 1h/C₆₀ repeat
3) C₆₀ huge
4) C₇₀ also

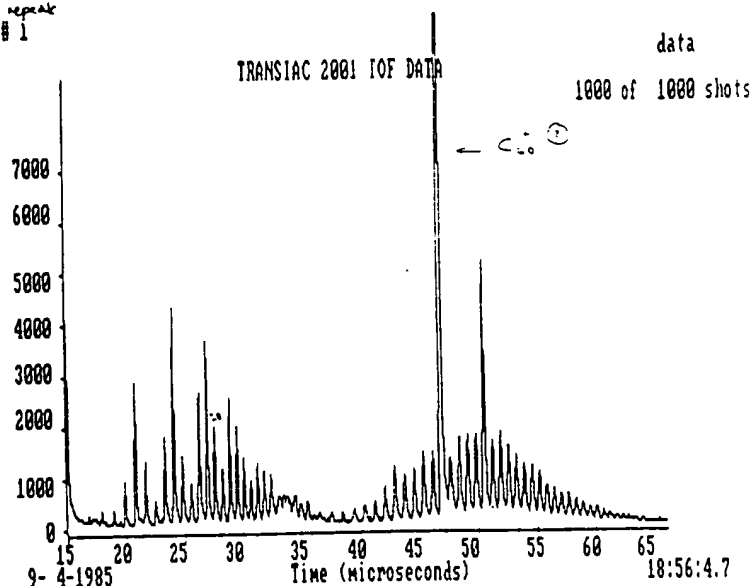


Figure 5. Time-of-flight mass spectrum of carbon clusters produced by laser vaporization of graphite (Sept 4, 1985) under conditions which first exhibited the dominance of the C₆₀ cluster and led to the recognition that 60 might be a "magic" number.

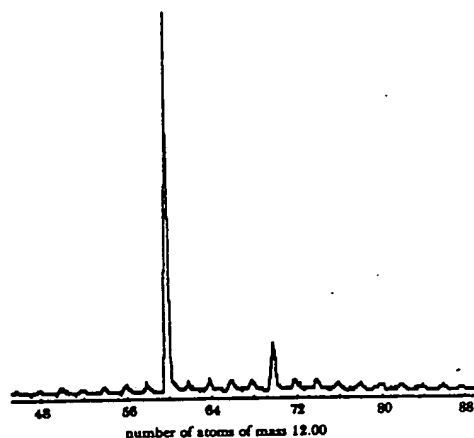


Figure 6. Time-of-flight mass spectrum carbon clusters produced by laser vaporization of graphite under the optimum conditions for observation of a dominant C₆₀ cluster signal.³ Note also the prominence of C₇₀.

conditions were found in which a ratio of 20/1 or more was achieved (Figure 6). It was soon realized that although C₆₀ generally appeared fairly special, the conditions under which it appeared dominant were rather unusual. They were conditions in which the major fraction of the carbon had nucleated to form macroscopic particles too large to be detectable by the mass spectrometer. Thus it was recognized that the signal shown in Figure 6 shows the "small" carbon species which remain when the microparticles have formed. Due to the fact that geodesic structural concepts were a guide to the hollow cage structural explanation that

Hentriacontacyclo[29.29.0.0^{1,14}.0^{2,13}.0^{3,10}.0^{4,9}.0^{5,18}.0^{6,17}.0^{7,16}.0^{8,25}.0^{9,24}.0^{10,23}.0^{11,22}.0^{12,21}.0^{13,20}.0^{14,19}.0^{15,28}.0^{16,27}.0^{17,26}.0^{18,25}.0^{19,24}.0^{20,23}.0^{21,22}.0^{22,21}.0^{23,20}.0^{24,19}.0^{25,18}.0^{26,17}.0^{27,16}.0^{28,15}.0^{29,14}.0^{30,13}.0^{31,12}.0^{32,11}.0^{33,10}.0^{34,9}.0^{35,8}.0^{36,7}.0^{37,6}.0^{38,5}.0^{39,4}.0^{40,3}.0^{41,2}.0^{42,1}.0^{43,0}.0^{44,0}.0^{45,0}.0^{46,0}.0^{47,0}.0^{48,0}.0^{49,0}.0^{50,0}.0^{51,0}.0^{52,0}.0^{53,0}.0^{54,0}.0^{55,0}.0^{56,0}.0^{57,0}.0^{58,0}.0^{59,0}.0^{60,0}.0^{61,0}.0^{62,0}.0^{63,0}.0^{64,0}.0^{65,0}.0^{66,0}.0^{67,0}.0^{68,0}.0^{69,0}.0^{70,0}.0^{71,0}.0^{72,0}.0^{73,0}.0^{74,0}.0^{75,0}.0^{76,0}.0^{77,0}.0^{78,0}.0^{79,0}.0^{80,0}.0^{81,0}.0^{82,0}.0^{83,0}.0^{84,0}.0^{85,0}.0^{86,0}.0^{87,0}.0^{88,0}.0^{89,0}.0^{90,0}.0^{91,0}.0^{92,0}.0^{93,0}.0^{94,0}.0^{95,0}.0^{96,0}.0^{97,0}.0^{98,0}.0^{99,0}.0^{100,0}.0^{101,0}.0^{102,0}.0^{103,0}.0^{104,0}.0^{105,0}.0^{106,0}.0^{107,0}.0^{108,0}.0^{109,0}.0^{110,0}.0^{111,0}.0^{112,0}.0^{113,0}.0^{114,0}.0^{115,0}.0^{116,0}.0^{117,0}.0^{118,0}.0^{119,0}.0^{120,0}.0^{121,0}.0^{122,0}.0^{123,0}.0^{124,0}.0^{125,0}.0^{126,0}.0^{127,0}.0^{128,0}.0^{129,0}.0^{130,0}.0^{131,0}.0^{132,0}.0^{133,0}.0^{134,0}.0^{135,0}.0^{136,0}.0^{137,0}.0^{138,0}.0^{139,0}.0^{140,0}.0^{141,0}.0^{142,0}.0^{143,0}.0^{144,0}.0^{145,0}.0^{146,0}.0^{147,0}.0^{148,0}.0^{149,0}.0^{150,0}.0^{151,0}.0^{152,0}.0^{153,0}.0^{154,0}.0^{155,0}.0^{156,0}.0^{157,0}.0^{158,0}.0^{159,0}.0^{160,0}.0^{161,0}.0^{162,0}.0^{163,0}.0^{164,0}.0^{165,0}.0^{166,0}.0^{167,0}.0^{168,0}.0^{169,0}.0^{170,0}.0^{171,0}.0^{172,0}.0^{173,0}.0^{174,0}.0^{175,0}.0^{176,0}.0^{177,0}.0^{178,0}.0^{179,0}.0^{180,0}.0^{181,0}.0^{182,0}.0^{183,0}.0^{184,0}.0^{185,0}.0^{186,0}.0^{187,0}.0^{188,0}.0^{189,0}.0^{190,0}.0^{191,0}.0^{192,0}.0^{193,0}.0^{194,0}.0^{195,0}.0^{196,0}.0^{197,0}.0^{198,0}.0^{199,0}.0^{200,0}.0^{201,0}.0^{202,0}.0^{203,0}.0^{204,0}.0^{205,0}.0^{206,0}.0^{207,0}.0^{208,0}.0^{209,0}.0^{210,0}.0^{211,0}.0^{212,0}.0^{213,0}.0^{214,0}.0^{215,0}.0^{216,0}.0^{217,0}.0^{218,0}.0^{219,0}.0^{220,0}.0^{221,0}.0^{222,0}.0^{223,0}.0^{224,0}.0^{225,0}.0^{226,0}.0^{227,0}.0^{228,0}.0^{229,0}.0^{230,0}.0^{231,0}.0^{232,0}.0^{233,0}.0^{234,0}.0^{235,0}.0^{236,0}.0^{237,0}.0^{238,0}.0^{239,0}.0^{240,0}.0^{241,0}.0^{242,0}.0^{243,0}.0^{244,0}.0^{245,0}.0^{246,0}.0^{247,0}.0^{248,0}.0^{249,0}.0^{250,0}.0^{251,0}.0^{252,0}.0^{253,0}.0^{254,0}.0^{255,0}.0^{256,0}.0^{257,0}.0^{258,0}.0^{259,0}.0^{260,0}.0^{261,0}.0^{262,0}.0^{263,0}.0^{264,0}.0^{265,0}.0^{266,0}.0^{267,0}.0^{268,0}.0^{269,0}.0^{270,0}.0^{271,0}.0^{272,0}.0^{273,0}.0^{274,0}.0^{275,0}.0^{276,0}.0^{277,0}.0^{278,0}.0^{279,0}.0^{280,0}.0^{281,0}.0^{282,0}.0^{283,0}.0^{284,0}.0^{285,0}.0^{286,0}.0^{287,0}.0^{288,0}.0^{289,0}.0^{290,0}.0^{291,0}.0^{292,0}.0^{293,0}.0^{294,0}.0^{295,0}.0^{296,0}.0^{297,0}.0^{298,0}.0^{299,0}.0^{300,0}.0^{301,0}.0^{302,0}.0^{303,0}.0^{304,0}.0^{305,0}.0^{306,0}.0^{307,0}.0^{308,0}.0^{309,0}.0^{310,0}.0^{311,0}.0^{312,0}.0^{313,0}.0^{314,0}.0^{315,0}.0^{316,0}.0^{317,0}.0^{318,0}.0^{319,0}.0^{320,0}.0^{321,0}.0^{322,0}.0^{323,0}.0^{324,0}.0^{325,0}.0^{326,0}.0^{327,0}.0^{328,0}.0^{329,0}.0^{330,0}.0^{331,0}.0^{332,0}.0^{333,0}.0^{334,0}.0^{335,0}.0^{336,0}.0^{337,0}.0^{338,0}.0^{339,0}.0^{340,0}.0^{341,0}.0^{342,0}.0^{343,0}.0^{344,0}.0^{345,0}.0^{346,0}.0^{347,0}.0^{348,0}.0^{349,0}.0^{350,0}.0^{351,0}.0^{352,0}.0^{353,0}.0^{354,0}.0^{355,0}.0^{356,0}.0^{357,0}.0^{358,0}.0^{359,0}.0^{360,0}.0^{361,0}.0^{362,0}.0^{363,0}.0^{364,0}.0^{365,0}.0^{366,0}.0^{367,0}.0^{368,0}.0^{369,0}.0^{370,0}.0^{371,0}.0^{372,0}.0^{373,0}.0^{374,0}.0^{375,0}.0^{376,0}.0^{377,0}.0^{378,0}.0^{379,0}.0^{380,0}.0^{381,0}.0^{382,0}.0^{383,0}.0^{384,0}.0^{385,0}.0^{386,0}.0^{387,0}.0^{388,0}.0^{389,0}.0^{390,0}.0^{391,0}.0^{392,0}.0^{393,0}.0^{394,0}.0^{395,0}.0^{396,0}.0^{397,0}.0^{398,0}.0^{399,0}.0^{400,0}.0^{401,0}.0^{402,0}.0^{403,0}.0^{404,0}.0^{405,0}.0^{406,0}.0^{407,0}.0^{408,0}.0^{409,0}.0^{410,0}.0^{411,0}.0^{412,0}.0^{413,0}.0^{414,0}.0^{415,0}.0^{416,0}.0^{417,0}.0^{418,0}.0^{419,0}.0^{420,0}.0^{421,0}.0^{422,0}.0^{423,0}.0^{424,0}.0^{425,0}.0^{426,0}.0^{427,0}.0^{428,0}.0^{429,0}.0^{430,0}.0^{431,0}.0^{432,0}.0^{433,0}.0^{434,0}.0^{435,0}.0^{436,0}.0^{437,0}.0^{438,0}.0^{439,0}.0^{440,0}.0^{441,0}.0^{442,0}.0^{443,0}.0^{444,0}.0^{445,0}.0^{446,0}.0^{447,0}.0^{448,0}.0^{449,0}.0^{450,0}.0^{451,0}.0^{452,0}.0^{453,0}.0^{454,0}.0^{455,0}.0^{456,0}.0^{457,0}.0^{458,0}.0^{459,0}.0^{460,0}.0^{461,0}.0^{462,0}.0^{463,0}.0^{464,0}.0^{465,0}.0^{466,0}.0^{467,0}.0^{468,0}.0^{469,0}.0^{470,0}.0^{471,0}.0^{472,0}.0^{473,0}.0^{474,0}.0^{475,0}.0^{476,0}.0^{477,0}.0^{478,0}.0^{479,0}.0^{480,0}.0^{481,0}.0^{482,0}.0^{483,0}.0^{484,0}.0^{485,0}.0^{486,0}.0^{487,0}.0^{488,0}.0^{489,0}.0^{490,0}.0^{491,0}.0^{492,0}.0^{493,0}.0^{494,0}.0^{495,0}.0^{496,0}.0^{497,0}.0^{498,0}.0^{499,0}.0^{500,0}.0^{501,0}.0^{502,0}.0^{503,0}.0^{504,0}.0^{505,0}.0^{506,0}.0^{507,0}.0^{508,0}.0^{509,0}.0^{510,0}.0^{511,0}.0^{512,0}.0^{513,0}.0^{514,0}.0^{515,0}.0^{516,0}.0^{517,0}.0^{518,0}.0^{519,0}.0^{520,0}.0^{521,0}.0^{522,0}.0^{523,0}.0^{524,0}.0^{525,0}.0^{526,0}.0^{527,0}.0^{528,0}.0^{529,0}.0^{530,0}.0^{531,0}.0^{532,0}.0^{533,0}.0^{534,0}.0^{535,0}.0^{536,0}.0^{537,0}.0^{538,0}.0^{539,0}.0^{540,0}.0^{541,0}.0^{542,0}.0^{543,0}.0^{544,0}.0^{545,0}.0^{546,0}.0^{547,0}.0^{548,0}.0^{549,0}.0^{550,0}.0^{551,0}.0^{552,0}.0^{553,0}.0^{554,0}.0^{555,0}.0^{556,0}.0^{557,0}.0^{558,0}.0^{559,0}.0^{560,0}.0^{561,0}.0^{562,0}.0^{563,0}.0^{564,0}.0^{565,0}.0^{566,0}.0^{567,0}.0^{568,0}.0^{569,0}.0^{570,0}.0^{571,0}.0^{572,0}.0^{573,0}.0^{574,0}.0^{575,0}.0^{576,0}.0^{577,0}.0^{578,0}.0^{579,0}.0^{580,0}.0^{581,0}.0^{582,0}.0^{583,0}.0^{584,0}.0^{585,0}.0^{586,0}.0^{587,0}.0^{588,0}.0^{589,0}.0^{590,0}.0^{591,0}.0^{592,0}.0^{593,0}.0^{594,0}.0^{595,0}.0^{596,0}.0^{597,0}.0^{598,0}.0^{599,0}.0^{600,0}.0^{601,0}.0^{602,0}.0^{603,0}.0^{604,0}.0^{605,0}.0^{606,0}.0^{607,0}.0^{608,0}.0^{609,0}.0^{610,0}.0^{611,0}.0^{612,0}.0^{613,0}.0^{614,0}.0^{615,0}.0^{616,0}.0^{617,0}.0^{618,0}.0^{619,0}.0^{620,0}.0^{621,0}.0^{622,0}.0^{623,0}.0^{624,0}.0^{625,0}.0^{626,0}.0^{627,0}.0^{628,0}.0^{629,0}.0^{630,0}.0^{631,0}.0^{632,0}.0^{633,0}.0^{634,0}.0^{635,0}.0^{636,0}.0^{637,0}.0^{638,0}.0^{639,0}.0^{640,0}.0^{641,0}.0^{642,0}.0^{643,0}.0^{644,0}.0^{645,0}.0^{646,0}.0^{647,0}.0^{648,0}.0^{649,0}.0^{650,0}.0^{651,0}.0^{652,0}.0^{653,0}.0^{654,0}.0^{655,0}.0^{656,0}.0^{657,0}.0^{658,0}.0^{659,0}.0^{660,0}.0^{661,0}.0^{662,0}.0^{663,0}.0^{664,0}.0^{665,0}.0^{666,0}.0^{667,0}.0^{668,0}.0^{669,0}.0^{670,0}.0^{671,0}.0^{672,0}.0^{673,0}.0^{674,0}.0^{675,0}.0^{676,0}.0^{677,0}.0^{678,0}.0^{679,0}.0^{680,0}.0^{681,0}.0^{682,0}.0^{683,0}.0^{684,0}.0^{685,0}.0^{686,0}.0^{687,0}.0^{688,0}.0^{689,0}.0^{690,0}.0^{691,0}.0^{692,0}.0^{693,0}.0^{694,0}.0^{695,0}.0^{696,0}.0^{697,0}.0^{698,0}.0^{699,0}.0^{700,0}.0^{701,0}.0^{702,0}.0^{703,0}.0^{704,0}.0^{705,0}.0^{706,0}.0^{707,0}.0^{708,0}.0^{709,0}.0^{710,0}.0^{711,0}.0^{712,0}.0^{713,0}.0^{714,0}.0^{715,0}.0^{716,0}.0^{717,0}.0^{718,0}.0^{719,0}.0^{720,0}.0^{721,0}.0^{722,0}.0^{723,0}.0^{724,0}.0^{725,0}.0^{726,0}.0^{727,0}.0^{728,0}.0^{729,0}.0^{730,0}.0^{731,0}.0^{732,0}.0^{733,0}.0^{734,0}.0^{735,0}.0^{736,0}.0^{737,0}.0^{738,0}.0^{739,0}.0^{740,0}.0^{741,0}.0^{742,0}.0^{743,0}.0^{744,0}.0^{745,0}.0^{746,0}.0^{747,0}.0^{748,0}.0^{749,0}.0^{750,0}.0^{751,0}.0^{752,0}.0^{753,0}.0^{754,0}.0^{755,0}.0^{756,0}.0^{757,0}.0^{758,0}.0^{759,0}.0^{760,0}.0^{761,0}.0^{762,0}.0^{763,0}.0^{764,0}.0^{765,0}.0^{766,0}.0^{767,0}.0^{768,0}.0^{769,0}.0^{770,0}.0^{771,0}.0^{772,0}.0^{773,0}.0^{774,0}.0^{775,0}.0^{776,0}.0^{777,0}.0^{778,0}.0^{779,0}.0^{780,0}.0^{781,0}.0^{782,0}.0^{783,0}.0^{784,0}.0^{785,0}.0^{786,0}.0^{787,0}.0^{788,0}.0^{789,0}.0^{790,0}.0^{791,0}.0^{792,0}.0^{793,0}.0^{794,0}.0^{795,0}.0^{796,0}.0^{797,0}.0^{798,0}.0^{799,0}.0^{800,0}.0^{801,0}.0^{802,0}.0^{803,0}.0^{804,0}.0^{805,0}.0^{806,0}.0^{807,0}.0^{808,0}.0^{809,0}.0^{810,0}.0^{811,0}.0^{812,0}.0^{813,0}.0^{814,0}.0^{815,0}.0^{816,0}.0^{817,0}.0^{818,0}.0^{819,0}.0^{820,0}.0^{821,0}.0^{822,0}.0^{823,0}.0^{824,0}.0^{825,0}.0^{826,0}.0^{827,0}.0^{828,0}.0^{829,0}.0^{830,0}.0^{831,0}.0^{832,0}.0^{833,0}.0^{834,0}.0^{835,0}.0^{836,0}.0^{837,0}.0^{838,0}.0^{839,0}.0^{840,0}.0^{841,0}.0^{842,0}.0^{843,0}.0^{844,0}.0^{845,0}.0^{846,0}.0^{847,0}.0^{848,0}.0^{849,0}.0^{850,0}.0^{851,0}.0^{852,0}.0^{853,0}.0^{854,0}.0^{855,0}.0^{856,0}.0^{857,0}.0^{858,0}.0^{859,0}.0^{860,0}.0^{861,0}.0^{862,0}.0^{863,0}.0^{864,0}.0^{865,0}.0^{866,0}.0^{867,0}.0^{868,0}.0^{869,0}.0^{870,0}.0^{871,0}.0^{872,0}.0^{873,0}.0^{874,0}.0^{875,0}.0^{876,0}.0^{877,0}.0^{878,0}.0^{879,0}.0^{880,0}.0^{881,0}.0^{882,0}.0^{883,0}.0^{884,0}.0^{885,0}.0^{886,0}.0^{887,0}.0^{888,0}.0^{889,0}.0^{890,0}.0^{891,0}.0^{892,0}.0^{893,0}.0^{894,0}.0^{895,0}.0^{896,0}.0^{897,0}.0^{898,0}.0^{899,0}.0^{900,0}.0^{901,0}.0^{902,0}.0^{903,0}.0^{904,0}.0^{905,0}.0^{906,0}.0^{907,0}.0^{908,0}.0^{909,0}.0^{910,0}.0^{911,0}.0^{912,0}.0^{913,0}.0^{914,0}.0^{915,0}.0^{916,0}.0^{917,0}.0^{918,0}.0^{919,0}.0^{920,0}.0^{921,0}.0^{922,0}.0^{923,0}.0^{924,0}.0^{925,0}.0^{926,0}.0^{927,0}.0^{928,0}.0^{929,0}.0^{930,0}.0^{931,0}.0^{932,0}.0^{933,0}.0^{934,0}.0^{935,0}.0^{936,0}.0^{937,0}.0^{938,0}.0^{939,0}.0^{940,0}.0^{941,0}.0^{942,0}.0^{943,0}.0^{944,0}.0^{945,0}.0^{946,0}.0^{947,0}.0^{948,0}.0^{949,0}.0^{950,0}.0^{951,0}.0^{952,0}.0^{953,0}.0^{954,0}.0^{955,0}.0^{956,0}.0^{957,0}.0^{958,0}.0^{959,0}.0^{960,0}.0^{961,0}.0^{962,0}.0^{963,0}.0^{964,0}.0^{965,0}.0⁹⁶⁶

work has been carried out. Two complementary accounts covering many of the important general implications and experimental observations have been given by Kroto⁵⁰ and Curl and Smalley.⁵¹ More focused accounts have also been published dealing mainly with experimental observations.⁵²⁻⁵⁴ astrophysical implications,^{42,55-68} symmetry and structure considerations of fullerene-60, and the icosahedral giant fullerenes.^{49,69} The chemical implications have also been discussed by Kroto⁶¹ and Kroto and Walton.¹⁰ Hirota⁶² and Heath⁶³ discuss fullerene-60 as well as other novel carbon molecules.

IV. Sources of C_{60}

In the original work, which showed how conditions could be achieved to produce a signal in which the C_{60} peak was dominant, the pulsed nozzle/laser vaporization technique²⁶ was used to produce the clusters from a graphite target and photoionization TOF-MS used to detect them. The laser-produced plasma expanded into a high pressure (ca. 1–10 atm) of He and the target graphite surface was continually replenished so that the surface remained essentially flat. A nozzle extender was used to increase the clustering time prior to expansion to ca. 100 μ s and the high He pressure increased the nucleation rate. Although initially it was conjectured that perhaps graphitic sheet fragments might have been ablated from the graphite target and rearranged into the buckminsterfullerene structure, subsequent considerations suggested that C_{60} was more likely to have formed by nucleation from carbon vapor consisting, at least initially, of C atoms and very small carbon molecules.⁵² Negative ion distributions produced by crossing a laser with the cluster beam just as it exited the nozzle⁶⁴ have been studied, and the relationship between these and positive and negative ion distributions, obtained directly from the vaporization zone (i.e. without photoionization), has been discussed by Hahn et al.⁶⁵ and O'Brien et al.⁶⁶ The consensus of opinion was that C_{60} appeared to exhibit special behavior whether charged (positive or negative) or neutral and that the nucleation rate order was neutrals > cations > anions.⁶⁶ Very detailed discussion of the conditions under which C_{60} appears to be special has been given by Cox et al.⁶⁷ These studies are discussed in more detail in section V.

Carbon cluster distributions exhibiting dominant C_{60}^+ signals, can be produced in another way as O'Keefe, Ross, and Baronavski⁶⁸ and Pradel et al.⁶⁹ have shown using high vacuum TOF-MS. In these experiments the graphite target is inside the mass spectrometer vacuum system and remains stationary. After several laser pulses a hole is drilled in the graphite and nucleation appears to occur in the cavity. McElvany et al.,⁷⁰ using ICR-MS techniques, have shown that if the axis of the laser-drilled hole is aligned parallel to the trapping magnetic field a strong C_{60}^+ signal predominates in the mass spectrum. In a study of the small cluster distribution, McElvany, Dunlap, and O'Keefe⁷¹ found that the vaporization of a diamond target produces the same distribution as does graphite. This result indicates that the clusters appear to be produced by nucleation of atomic/molecular carbon vapor rather than by a process involving the ablation of bulk fragments from the target. Meier and Rathjens⁷² have modified the original laser

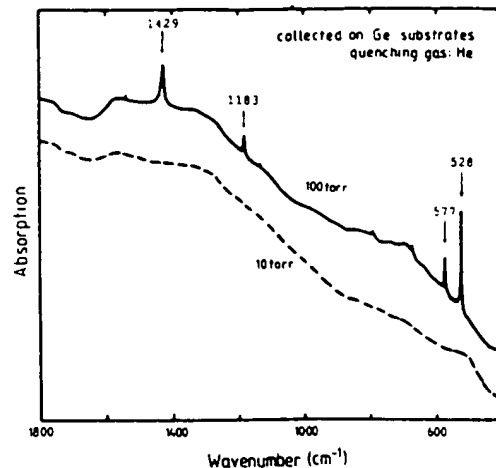


Figure 8. Infrared absorption spectrum observed in 1989 by Krätschmer, Fostiropoulos, and Huffman⁵⁷⁴ from carbon produced by arc-discharge processing. Krätschmer et al. made the perceptive observation that the four sharp absorption features indicated might belong to fullerene-60. The frequencies were tantalizingly consistent with theoretical predictions (section VIII) for the fundamental vibrations of fullerene-60 (reprinted from ref 74; copyright 1990 Elsevier Science Publishers).

vaporization procedure for producing C_{60} ³ in order to deposit material on a film. They have shown that the mass spectrum obtained by subsequent laser desorption of the resulting material yields a very similar cluster distribution to that of the cluster beam experiments. They have also carried out isotope scrambling measurements⁷³ supporting the conclusion that C_{60} is assembled from small carbon species in the gas phase after vaporization (see section VI).

A fascinating and ultimately key observation was described in September 1989 by the Heidelberg/Tucson group: Krätschmer, Fostiropoulos, and Huffman⁵⁷⁴ who detected four weak bands in the infrared spectrum of a film deposited from a carbon arc under argon (Figure 8). Krätschmer et al. pointed out that the vibrational frequencies of the four bands (and associated ¹³C shifts) observed were in tantalizingly close agreement with theoretical estimates for fullerene-60 (details in sections VIII and IX).

Several other interesting studies have shown that laser vaporization of a wide variety of carbonaceous target materials (other than pure carbon) also yields a dominant C_{60} signal: e.g. carbon films (Creasy and Brenna⁷⁵), polymers such as polyimides (Creasy and Brenna,⁷⁶ and Cambell et al.⁷⁷⁻⁷⁹), coal (Greenwood et al.⁸⁰), polycyclic aromatic hydrocarbons (Giardini-Guidoni et al.,⁸¹ and Lineman et al.^{82,83}). Last but not least, So and Wilkins⁸⁴ have shown that C_{60} can be detected by laser desorption of soot! In fact they have observed even-numbered carbon clusters with as many as 600 carbon atoms (Figure 9). This result and similar experiments may indicate that giant fullerenes may also be forming.⁶⁰ All experiments show that conditions can be found in which the C_{60}^+ peak is either prominent or dominant. However conditions also exist for which this is not the case.⁸⁴ It is likely that the availability of many other pathways to "organic" (H-containing species) may be responsible for some of the latter observations.

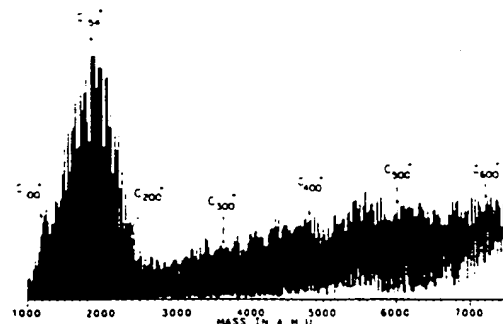


Figure 9. Laser desorption Fourier transform mass spectrum, observed by So and Wilkins,⁸⁴ of soot deposited on a KCl-coated stainless steel probe tip. Note that all the peaks here also correspond to even numbered carbon species. Since only even-numbered carbon aggregates can close perfectly it is possible that the explanation for this phenomenon is that these species are fullerenes and that the larger species are giant fullerenes of the kind depicted in Figure 22.

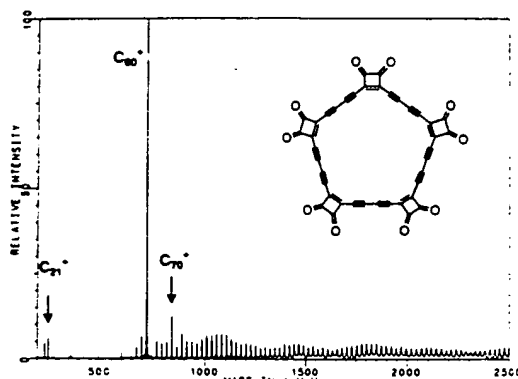


Figure 10. Remarkable positive-ion laser desorption Fourier transform mass spectrum, observed by Rubin et al.,⁸⁵ of the ring carbon oxide depicted under low laser power. This oxide which might be expected to decarbonylate to yield a C_{30} monocyclic ring has clearly dimerized to form C_{60} buckminsterfullerene!

A most exciting result was described by Rubin et al.⁸⁵ who have used a combination of organic synthesis and laser desorption mass spectrometry. In a preliminary study by the same group (Diederich et al.⁸⁶) attempted to prepare pure carbon rings, a prominent peak for the C_{18} cluster was detected during mass spectrometric analysis of a laser desorbed 18-carbon ring precursor. This work has now been advanced in spectacular fashion; refined measurements on C_{18} and C_{24} precursors⁸⁵ yield mass spectra which show prominent C_{60} and C_{70} signals. However most striking is the observation that laser desorption of the C_{30} ring precursor produces a mass spectrum containing a totally dominant C_{60} signal! (Figure 10). This result suggests that, in the vapor phase, a spectacular dimerization process occurs in which two C_{30} polyyne/cumulene rings combine in a concerted folding rearrangement to form the C_{60} cage.¹⁰ The implications of this process and indeed other aspects of the fullerene discovery for organic chemistry have been considered.^{10,61}

Some of the most important of all these experiments were those of Homann and co-workers⁸⁷⁻⁹⁰ who detected

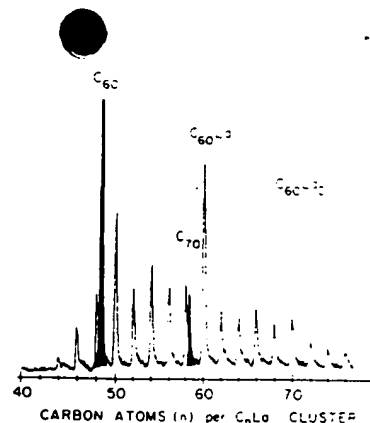


Figure 11. Mass spectrum of $C_{60}La$ cluster complexes and bare C_n clusters as observed by Heath et al.⁷ when $LaCl_3$ -doped graphite is laser vaporized (ArF 6.5 eV, 10 mJ cm⁻²). Note the particularly strong peak for $C_{60}La$ and the absence of a peak for $C_{60}La_2$. This result is discussed in section VI (adapted from ref. 7).

C_{60}^+ in a sooting flame. These observations are discussed in more detail in section VII.

V. Stability and Intrinsic Properties of C_{60}

After the buckminsterfullerene structure was proposed³ the intrinsic properties of the species were probed by the Rice/Sussex group.⁵⁰⁻⁵⁴ It was clearly vital to determine how reliable the experimental observation of the "stability" of the C_{60} cluster was, i.e. how "special" or "magic" the cluster actually was and how certain one could be about the buckminsterfullerene hollow cage explanation. After all, the proposal appeared to rest entirely on the observation of a single, strong mass spectrum peak at 720 amu (Figures 5 and 6), and such highly circumstantial evidence needed further support. Mass spectrometry is particularly susceptible to erroneous conclusions drawn on the basis of magic numbers due to the likely presence of ionization and fragmentation artifacts. Various aspects of the original experiment led to the conclusion that the cation mass spectrum (Figures 5 and 6) was most probably an accurate reflection of the neutral cluster distribution. Nevertheless it was necessary to carry out experiments in order to probe the behavior of C_{60} more deeply in order to generate further evidence, albeit still circumstantial, to support the stability conclusion and the cage structure proposal.

During the period from 1985 to 1990 many experiments were performed by a number of groups operating in the cluster field which probed carbon behavior with a view to confirming or falsifying the fullerene-60 proposal. If C_{60} really were a cage then the most obvious next step was to attempt to trap an atom inside the cage. The first result, in this context, was the observation of $C_{60}La$ by Heath et al.⁷ By using a graphite disk, soaked in $LaCl_3$ solution a strong signal was obtained for the monolanthanum complex $C_{60}La$, with no evidence of a peak for $C_{60}La_2$ (Figure 11). Cox et al.⁹¹ questioned the conclusion. They pointed out that, since C_{60} needs two 6.4 eV (ArF) photons for ionization and $C_{60}La$ only one, the relative strengths of the $C_{60}La^+$ and bare C_{60}^+ MS signals should not necessarily be taken as reliable gauges of their respective abundances, and a possible $C_{60}La_2^+$ signal might be too weak to detect

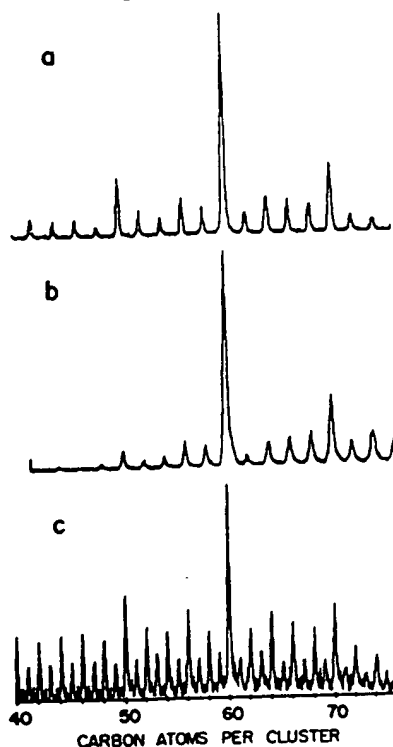


Figure 12. Carbon cluster ions observed under various production conditions⁴² (a) negative ions produced by directing a KrF excimer into the nozzle during expansion, (b) positive carbon cluster ions produced directly during vaporization in the nozzle without the aid of the KrF excimer laser, and (c) negative ions produced directly during vaporization in the nozzle, again without the aid of the KrF excimer laser but with longer residence time in the clustering region than in the case of the positive ions depicted in b (reprinted from ref 52; copyright 1987 Gordon and Breach Science Publishers, Inc.).

Cox et al.⁶⁷ have discussed further the cage hypothesis in general and metal atom encapsulation in particular and after detailed assessment they conclude that overall their observations are non-committal over whether C₆₀ was a cage or not.

For the smaller carbon species the positive ions display the well known magic numbers: 11, 15, 19, 23 (the so-called " $\Delta n = 4$ " effect, cf. Figure 4) whereas the negative ions exhibit a different sequence.^{21-24,1,2} The paper announcing the original discovery³ assumed that the mass spectra (Figures 5 and 6) reflected accurately neutral carbon cluster distributions. If the buckminsterfullerene structural proposal were correct however, the positive and negative ion distributions would be expected to exhibit a similar prominence for the 60-carbon atom analogue. The first experiment to probe this possibility⁶⁴ showed that negative ions, produced by laser ionization just after the cluster beam exited from the nozzle exhibited an anion mass spectrum in which C₆₀⁻ was dominant. In this experiment the neutral species became negatively charged by electron transfer. If the positive or negative ions, produced directly by vaporization are studied, it is found that only after clustering is allowed to continue for a

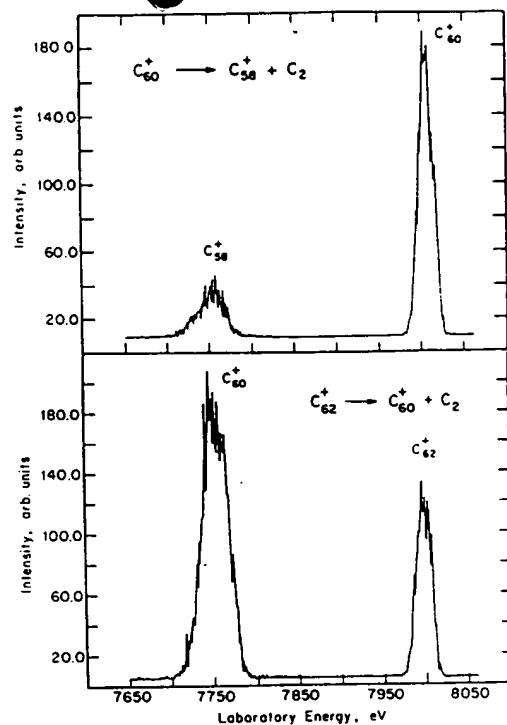


Figure 13. Metastable mass-analyzed ion kinetic energy scans (MIKES) published by Radi et al.⁵⁰ The parent ion (on the right) is mass selected by the magnetic analyzer and the horizontal axis is a scan of the electrostatic analyzer voltage. The parent ion energy is 8 keV. C₂ loss is observed from C₆₀⁺ (above) and C₆₂⁺ (below). Note the dramatic differences in metastable activity as reflected by the relative intensities of the product peaks, relative to their parent ions in these two cases (reprinted from ref 93; copyright 1990 the American Institute of Physics).

significant length of time is the C₆₀⁻ anion dominant⁶⁶ otherwise it is not.⁶⁵ Some examples of mass spectra recorded under various conditions^{51,64,66} are presented in Figure 12. Cox, Reichmann, and Kaldor⁶⁷ describe some intriguing relative time-of-flight differences in behavior between various individual clusters, in particular C₂₈ and C₆₀, which are highly dependent on the nozzle parameters. These experiments appear to suggest that wall reactions may occur in the nucleation channel. It is possible that what was observed in this experiment was C₆₀ deposited in the channel which subsequently desorbed. The main evidence for the importance of wall effects lies in the detection of C₆₀K clusters when a new, pure (i.e. K free) carbon target replaces a previous one doped with potassium.

Important observations have had a bearing on the stability of C₆₀. The very early experiments by Bloomfield et al.²⁸ showed that C₆₀ was susceptible to multiphoton fragmentation. A series of studies by Bowers and co-workers²²⁻²⁴ showed that C₆₀ could undergo metastable fragmentation. Particularly interesting is the observation that C₆₀ exhibits much lower metastability than other neighboring clusters such as C₅₈ as shown in Figure 13. These results suggest that hot C₆₀ may exhibit phenomena associated with fluidity—perhaps an intriguing form of surface fluidity. On the

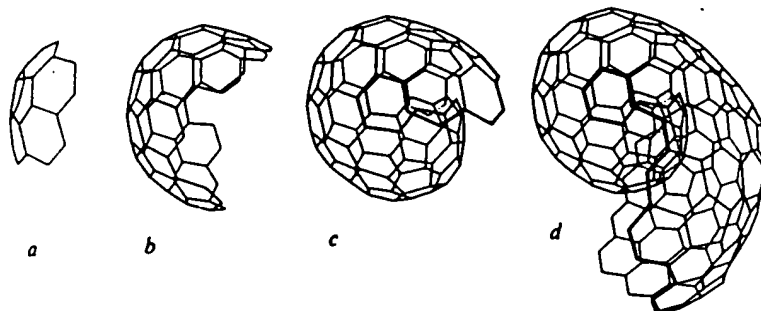


Figure 17. Diagrammatic representation¹⁰⁸ of a hypothetical carbon vapor nucleation scheme^{103,106} proposed for the formation of concentric shell graphite microparticles. Note that the structure c has overlapped and so trapped the trailing edge inside the spiraling network. This species is thus essentially the embryo for further growth. It is proposed that C₆₀ might be produced by a modification of this process in which the edges meet and seal to form a closed cage. In such a case further growth by chemical bond formation might be expected to be halted. It was conjectured that similar structures might occur as intermediates during soot nucleation (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

ArF and 1-photon ionized by F₂.^{103,67}

As mentioned in section IV, the most intriguing and convincing spectra were those obtained in the infrared study of Krätschmer, Fostiropoulos, and Huffman in 1990^{5,74} (see further details in sections VIII and IX).

VI. Reaction Studies

The first reaction studies aimed at probing the cage concept were those of Heath et al.⁷ and Cox et al.^{91,67} (discussed in section V) who studied the carbon/metal complexes. Rohlfsing et al.²⁵ and Heath et al.^{29,30} carried out similar reaction studies which focused mainly on the properties of the carbon chains. It is also important to note that van der Waals complexes can form in the supersonic beam if C₆₀ is cold.

When various gases such as CO, NO, and SO₂ were introduced into a reactor, placed downstream from the nozzle in which C₆₀ is formed, Zhang et al.¹⁰³ showed that all the even carbon clusters were totally unreactive. The odd clusters were, on the other hand, very reactive. These experiments gained significant further support from the studies of McElvany et al.⁷⁰ and Weiss et al.⁹⁶ which showed C₆₀ and its analogues to be extremely unreactive in an ICR trap. However if gases are mixed with the driver gas in the nozzle, reactions can take place before and after C₆₀ is formed. With hydrogen, a wide range of hydrocarbon products is detected (Rohlfsing,¹⁰⁴ Hallett et al.,¹⁰⁵ and Doverstal et al.¹⁰⁶). Rohlfsing has used an in-line reflectron modification of the cluster beam technique and made some very careful high-resolution mass spectrometric measurements of the reactions of clusters C₂₀–C₈₀ with hydrogen.¹⁰⁴ The variations in reactivity appear to be structure related and consistent with the cage proposal. The study suggests that chain cluster species with as many as 44 carbon atoms may be present. Complementary experiments by Hallett et al.¹⁰⁵ and Doverstal et al.¹⁰⁶ indicate that clusters in the C₂₀–C₄₀ range show at least three different types of reactivity as evidenced by the mass spectrometric patterns of the hydrogenated products. The observations¹⁰⁶ are consistent with the proposal that small fullerenes (C₂₀, C₂₄, C₂₈, C₃₂, C₃₆) can form.⁸ They are also consistent with the fact that formation of no 22 atom fullerene can exist, as pointed out by Fowler and Steig¹⁰⁷

VII. Gas-Phase Carbon Nucleation and C₆₀ Formation

It would appear that most workers in the field are able to observe special behavior fairly easily and under a wide range of conditions, all of which have one major feature in common: C₆₀ appears to be dominant only when nucleation nears completion, leaving behind C₆₀ and other even-numbered relatives such as C₇₀. This result has one obviously simple explanation; at least some fraction of the even clusters—particularly C₆₀—is unreactive toward growth into macroscopic particles. The spontaneous creation of C₆₀ requires a mechanistic explanation. In particular, entropy factors clearly need to be carefully assessed when it is proposed that so symmetric an object is formed in a chaotic plasma. A feasible nucleation mechanism was provided by Zhang et al.¹⁰³ and refined further by Kroto and McKay.¹⁰⁸ The nucleation model proposes that curved sp²-linked (aromatic) carbon networks form (Figure 17) and can serve as embryos for further growth. The energetics of sheet carbon cluster radicals is invoked to explain the curvature/partial closure. Essentially the drive toward closure is governed by the energy released as a result of eliminating the edge dangling bonds. For instance a flat graphite-like sheet of 60 atoms would have at least 20 dangling bonds, whereas fullerene-60 would, of course, have none. In general, in a chaotic system, partly closed, overlapped embryos, such as that shown in Figure 16c, are expected to form and which, once overlapped, cannot close perfectly. These species are probably highly active nucleation sites to which permanent chemical binding of adsorbing fragments can take place. Of course some form of closure/annealing process might take place if the temperature is high enough for intra and extra network rearrangement to occur. It was proposed^{103,106} that during this general spiral nucleation process some embryos would close forming fullerenes, particularly fullerene-60 which would no longer present a site for efficient accretion. The process is primarily a physicochemical nucleation scheme in which the fullerenes act as deadends for the most rapid nucleation.

After embryo formation, epitaxial growth has been shown to result in icospiral graphitic giant molecules or microparticles¹⁰⁶ with structures consistent with

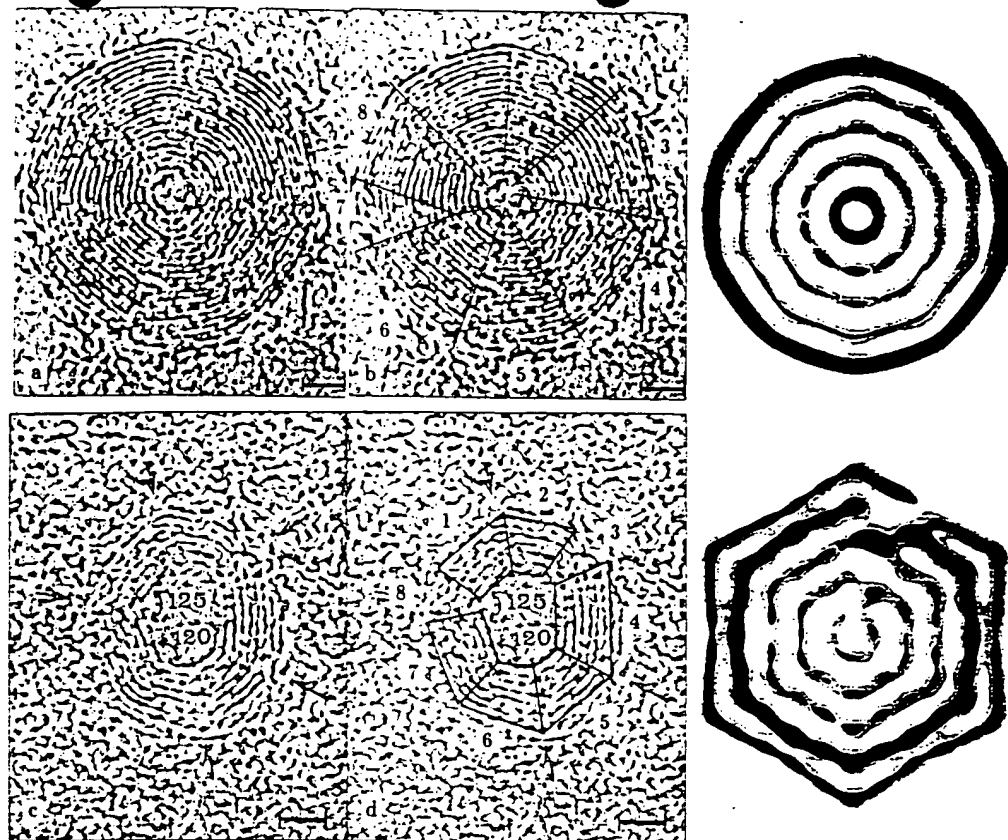


Figure 18. Comparison by McKay et al.^{111,112} between TEM images of polyhedral graphitic microparticles observed by Iijima¹⁰⁹ and simulated TEM images for a hypothetical spiral shell particle predicted by the nucleation scheme depicted in Figure 17. The fairly round particle observed by Iijima which is depicted in a and b is seen to exhibit a similar pattern to the simulation top right. On the other hand the more polygonal particle, shown in c and d, exhibits a similar pattern to the simulation shown bottom right. The simulations are for the same particle observed from different angles. The hypothetical particle has shell interconnections which can most easily be seen in the lower right simulation. In b and d the polygonal outlines are delineated.

those of spheroidal graphitic microparticles observed by Iijima in 1980.^{109,110} Kroto et al.^{111,112} have provided further support for the scheme in the form of TEM image simulations based on the icospiral concentric shell structure concept,¹⁰⁸ in excellent agreement with the Iijima images as depicted in Figure 18. Roulston et al.¹¹³ have shown that certain electronic and structural properties of amorphous semiconducting carbons can be explained on the basis of a spheroidal graphitic infrastructure, rather than by the traditional flat microstructure. Yacaman et al.^{114,115} have shown that FT power-spectra processed, electron microscope images of carbon microparticles appear to be consistent with the quasicosahedral spiral substructure.¹⁰⁸ Attention has been drawn to the fact that small graphitic microparticles actually consist of crystalline quasicosahedral graphitic cores surrounded by amorphous carbon surface layers.^{116,109} Interestingly, Iijima¹¹⁰ has shown that the TEM structure at the nucleus of one of the carbon microparticles, studied earlier¹⁰⁹ was consistent with the image expected if it were a C_{60} cage. With hindsight this result demands further serious investigation to see whether fullerene-60 can itself be encapsulated during

later stages of particle growth.

Wales¹¹⁷ has considered some statistical aspects of the growth dynamics of closed-cage structures and Bernholc and Phillips have discussed the kinetic factors involved in the growth of carbon clusters in general.¹¹⁸

It was also suggested that a modified form of the nucleation scheme, devised to account for the spontaneous creation of C_{60} , could also explain the spheroidal nature of soot.^{103,108,50,51,119} This proposal was criticized by Frenklach, Ebert, and co-workers¹²⁰⁻¹²³ who favor an earlier theory, which invokes the physical condensation of flat PAH molecules held together by van der Waals forces into coagulating liquid drops. However, Harris and Weiner point out how little has been firmly established about the soot formation mechanism.¹²⁴ It can in fact be demonstrated¹²⁵ that the new scheme is broadly consistent with kinetic, structural, and chemical observations made on soot and its formation process.

The new nucleation scheme predicts that some C_{60} should form as a byproduct^{103,108} of soot production. Subsequently Gerhardt, Löffler and Homann,⁸⁷⁻⁹⁰ in studies of the ions produced in a sooting flame, found conditions under which the mass spectrum shown in

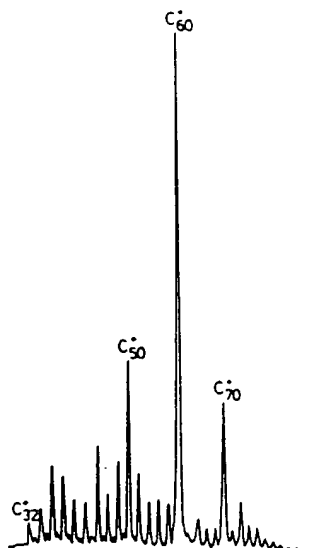


Figure 19. Mass spectrum, observed by Gerhardt, Löffler, and Homann,⁵⁷⁻⁶⁰ of positive ions produced by a sooting benzene-oxygen flame (C/O = 0.76) (reprinted from ref 87; copyright 1987 Elsevier Science Publishers).

Figure 19 is obtained. This spectrum is almost identical with that observed during the pure carbon laser vaporization experiments where C₆₀⁺ is the dominant ion! Homann and co-workers conclude that this observation should not be taken as support for the new spiral nucleation scenario as the tell-tale even ions with a dominant C₆₀⁺ peak are not seen until after the inception of soot particle formation. The carbon/hydrogen reaction studies¹⁰⁴⁻¹⁰⁶ promise to shed further light on the soot formation process, but the way in which the results might dovetail with the conventional data remains to be ascertained. Kroto has summarized the present state of affairs from this viewpoint.¹²⁵

VIII. Theoretical Studies of the Fullerenes

Theoretical studies predating the discovery of C₆₀ have been discussed in section II. After the discovery, theoreticians had a ball and many aspects of the molecule's properties have already been probed. The comprehensive overview of theoretical work on fullerene-60 presented by Weltner and Van Zee² is here conflated with more recent work.

One important aspect of the original experimental observations was the fact that C₇₀ also showed special

behavior. Topological and chemical stability arguments, as discussed by Kroto⁸ and Schmalz et al.,⁹ explain this observation as being entirely consistent with the fullerene proposal. Indeed these studies suggested that if the C₆₀ mass spectrometric signal were due to its having a closed cage fullerene structure, C₇₀ should show special behavior also, for the same reason. Thus, most importantly and rather convincingly, the fullerene structure proposal no longer rested on the single line observation. In fact it had now gained significant further support by the fact that a prediction had been made and neatly confirmed. Indeed the two observations, taken together, provided convincing evidence for the existence of a whole family of fullerenes and further probing suggested that in addition to C₆₀ and C₇₀, the C₂₄, C₂₈, C₃₂, and C₅₀ clusters (Figure 20) should also show varying degrees of special stability^{8,9} (N.B. fullerene-22 cannot exist¹⁰⁷).

The dominance of C₆₀ and C₇₀ was ascribed to the fact that these are the smallest fullerenes that can have an isomer (one in each case) in which none of the 12 pentagonal configurations, necessary and sufficient for closure, abut.^{8,9} It was shown^{8,50} that the predictions were commensurate with the mass spectrum obtained by Cox et al.⁶⁷ (Figure 21) and consequently there existed convincing experimental evidence for the fullerene family proposal. Since even-numbered carbon clusters are detectable with as many as 600 or more carbon atoms,⁸⁴ the possibility of giant fullerenes^{108,126} such as C₂₄₀ and C₅₄₀ shown in Figure 22 appears to be an exciting possibility.⁶⁰

Isomer stability has been discussed by Stone and Wales¹²⁷ who noted that the difference in energy between isomers is small and suggested that the C₆₀ signal should be due to a mixture of isomers. This result is difficult to reconcile with the observation (Figures 5 and 6) since it leads to the conclusion that C₆₀ is no more special than other clusters such as C₆₂. Potential energy functions have now been developed for the carbon cages systems by Takai et al.¹²⁸ and Balm et al.¹²⁹ The simulated annealing, Monte-Carlo methods used by Zerbetto¹³⁰ to study the behavior of small carbon clusters have been applied by Ballone and Milani¹³¹ in order to show that the fullerene cages are minimum energy structures.

A group theoretical analysis of the electronic properties of the fullerene family, by Fowler and Steer,¹⁰⁷ showed that the members, C_n where $n = 60 + 6k$ ($k = 0, 2, 3, 4, \dots$, i.e. an integer other than one), should have closed-shell electronic structures. The degree of aromaticity in a compound is of interest, and the number of Kekulé structures is often considered to be a guide. A total of 12 500 for fullerene-60 has been calculated

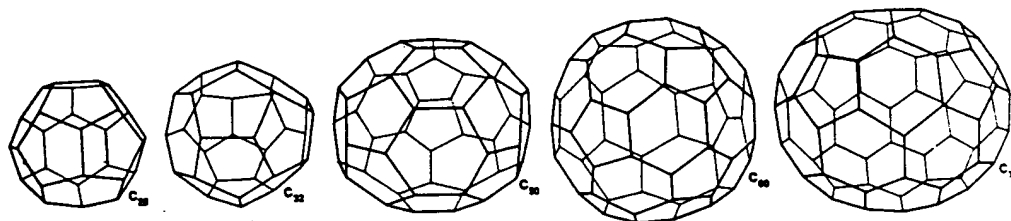


Figure 20. Five possible "magic" fullerenes predicted to display enhanced stability, relative to others in the range with 20-80 atoms, on the basis of chemical and geometric factors (reprinted from ref 8; copyright 1987 Macmillan Magazines Ltd).

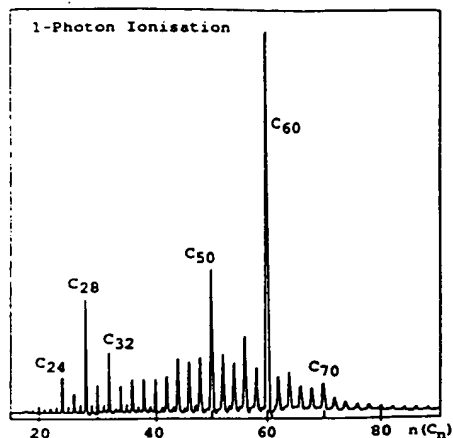


Figure 21. Time-of-flight mass spectrum taken from the data of Cox, Reichmann, and Kaldor.⁸⁷ The strong peaks are in excellent agreement with expectation⁴⁹ if they correspond to fullerenes. The fullerenes 24, 28, 32, 50, 60, and 70 (Figure 20) are predicted to exhibit enhanced stability, i.e. are magic. Note the sharp cutoff at C_{24} which is consistent with the fact that a no 22 atom fullerene can form.

by Schmalz et al.,¹³² Hosoya,¹³³ Brendsdal and Cyvin,¹³⁴ and by Elser.¹³⁵ Resonance circuit theory has been applied to this problem by Schmalz et al.,^{132,9} Klein et al.,^{136,137} as well as Randic, Nikolic, and Trinajstić.¹³⁸⁻¹⁴⁰ These studies indicate that account must be taken of the fact that some resonance structures make negative contributions to the aromatic stabilization. Schmalz et al.⁹ compared resonance circuit theory with Hückel molecular orbital (HMO) theory and concluded that C_{60} should be less aromatic than benzene. Amic and Trinajstić¹⁴⁰ discuss stabilization arising from bond delocalization. Graph theory has been applied to C_{60} and to other systems by Balasubramanian and Liu^{141,142} and also by Dias who has circumvented group theory in order to simplify Hückel calculations.¹⁴³ Hückel calculations on fullerene-60 have been made by Haymet^{144,20} and the stabilization due to delocalization discussed. Jiang and Zhang¹⁴⁵ have calculated the stability of fullerene-60 by Hückel theory using moment analysis techniques. Hess and Schaad¹⁴⁶ as well as

Aihara and Hosoya¹⁴⁷ have also applied Hückel theory to the problem, focusing on aspects of spheroidal aromaticity.

Fowler and Woolrich¹⁴⁸ have made three-dimensional HMO calculations which predict that C_{60} and C_{70} are closed shell systems. Fowler¹⁴⁹ extended this approach in order to assess the stability in other, larger fullerene cages, while Fowler, Cremona, and Steer¹⁵⁰ have discussed bonding in nonicosahedral spheroidal fullerene cages. Fowler¹⁵¹ has extended these ideas to various classes of cylindrical fullerenes and predicted closed electronic shells with an empty nonbonding orbital for clusters consisting of $10(7 + 3k)$ and $12(7 + 3k)$ atoms with 5- and 6-fold symmetry. Ceulemans and Fowler^{152,153} considered possible Jahn-Teller distortion pathways for icosahedral molecules.

Byers Brown¹⁵⁴ has discussed the simplification that high symmetry imparts to π -system calculations and obtained algebraic solutions for the orbital energies of fullerene-60. Electronic and vibrational properties were calculated by using a two-dimensional HMO method by Coulombeau and Rassat.¹⁵⁵ Semiempirical calculations including the effects of nonplanar π -orbital overlap due to curvature have also been carried out by using the free-electron model in the Coulson-Golubiewski, self-consistent Hückel approximation by Ozaki and Takahashi.¹⁵⁶ Haddon et al.^{157,158} have also considered the effects of nonplanarity, i.e. pyramidalization.

Extended Hückel calculations by Bocharov, Gal'pern, and Stankevich¹⁵⁹ and INDO and INDO/CI calculations by Feng et al.¹⁶⁰ have been applied to C_{60} and its isomers. A comparison between C_{60} and graphite was made by MNDO with geometry optimization by Newton and Stanton.¹⁶¹ McKee and Herndon¹⁶² also applied MNDO theory to cage carbons and concluded that the flat "graphitene" cage,¹⁴⁴ in which two coronene sheets are linked by pentagonal rings at the edge to form a disk-like structure should be more stable than fullerene-60. These authors also considered the mechanism of formation arising from rearrangement. Rehybridization and bonding were studied by Haddon, Brus, and Raghavachari who applied the π -orbital axis vector/3d-HMO (POAV/3D HMO) method^{157,158} and concluded that larger clusters were favored. It was also postulated that fullerene-240 should be more stable than C_{60} . Lüthi and Almlöf¹⁶³⁻¹⁶⁵ have carried out

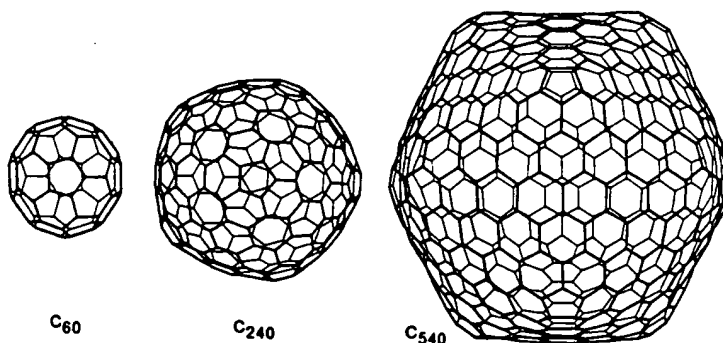


Figure 22. The set of fullerenes C_{60} , C_{240} , and C_{540} with diameters in the ratio 1:2:3. Kroto and McKay¹⁰⁸ showed that quasispherical shape develops rapidly for the giant fullerenes. Strain in the giant fullerenes is expected to be focused in the regions of the coronulene-like cusps. The surface thus becomes a smoothly curving network connecting the twelve cusps (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

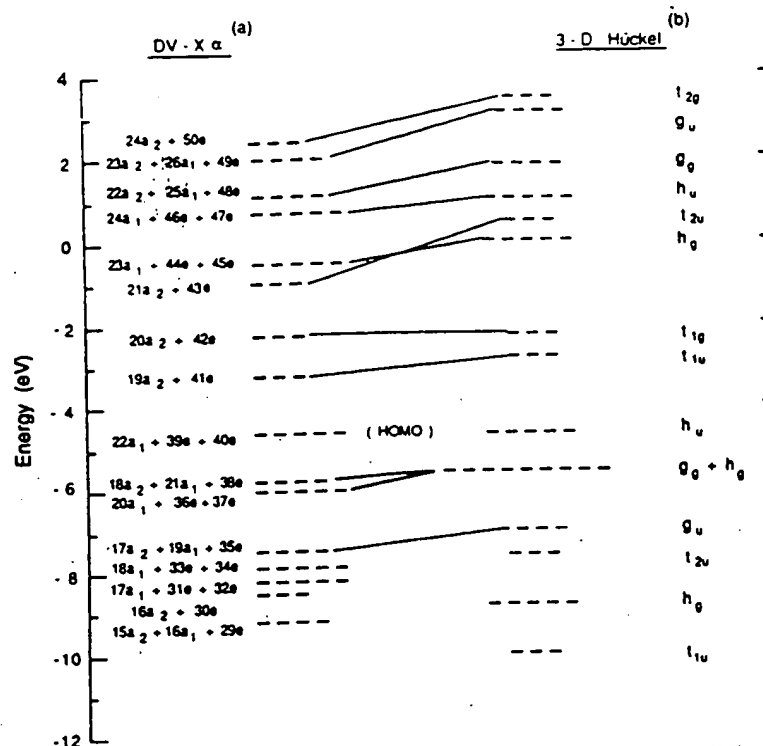


Figure 23. Orbital energy level diagram for fullerene-60 presented by Hale.¹⁶⁹ The energies derived by DV-X α calculations assuming D_5 symmetry on the left are compared with Hückel results. In the diagram β has been given the value -2.52 eV (reprinted from ref 169; copyright 1986 American Chemical Society).

large-scale restricted Hartree-Fock calculations and they deduced that $\Delta H_f = 415\text{--}490$ kcal/mol (relative to graphite) the electron affinity should be 0.8 eV and the ionization energy 7.92 eV. The electron affinity (2.4 eV) has been calculated by Larsson, Volosov, and Rosen¹⁶⁶ and by Braga et al.¹⁶⁷ Schulman and Disch¹⁶⁸ have calculated the heat of formation on the basis of ab initio SCF theory.

Hale¹⁶⁹ determined electronic properties, such as the ionization energy for fullerene-60, by the discrete variational (DV)-X α method using the Slater transition state formalism. Such calculations tend to be good for spheroidal systems. Hale's orbital energy level diagram for fullerene-60 is reproduced in Figure 23. The linear combination of muffin-tin orbital method in its atomic sphere approximation (LMTO ASA) was applied by Satpathy.¹⁷⁰ Calculations in which the partial retention of differential overlap PRDDO approach was applied were carried out by Marynick and Estreicher.¹⁷¹ Stone's tensor surface harmonic theory was used by Fowler and Woolrich.¹⁴⁸ The IMOA method (iterative maximum overlap approximation) was applied to a range of fullerenes by Kovacević, Graovac, and Babić¹⁷² to assess hybridization, structure and the amount of strain in these cages. Haddon¹⁷³ has discussed degree of pyramidalization considerations for fullerene-60 and other aromatic compounds.

Fabre and Rassat have reviewed the properties of known aromatic molecules which are essentially com-

In some of the calculations the electronic spectra of the fullerenes were the main focus. The calculations of Kataoka and Nakajima¹⁷⁵ and László and Udvardi¹⁷⁶ used the Pariser-Parr-Pople method (with CI) to determine spectra, structural parameters, and oscillator strengths. Optimized INDO calculations were published by Shibuya and Yoshitani.¹⁷⁷ The electronic structure and the spectra have also been studied by the CNDO/S method (including CI) by Larsson et al.¹⁶⁸ and by Braga et al.¹⁶⁷ Hayden and Mele¹⁷⁸ evaluated π -bonding behavior using the tight-binding model with electron-phonon coupling for the ground and excited states of fullerene-60. Jahn-Teller instabilities in the excited electronic states and the ion have been classified by Negri, Orlandi, and Zerbetto¹⁷⁹ who have also estimated Franck-Condon patterns and phosphorescence quantum yields.

Several calculations focused on the vibrational properties of fullerene-60. The result of primary (and historical) significance is that only four fundamentals are IR active due to the high symmetry of the molecule. Of the 174 vibrational modes giving rise to 42 fundamentals of various symmetries, four have t_{1u} symmetry and are IR active whereas 10 (eight h_g and two a_g) are Raman active.

Newton and Stanton¹⁸¹ gave preliminary details of the vibrational behavior of fullerene-60 using MNDO theory. A non-Cartesian coordinate method was employed to describe the C_{60} vibrations in terms of four-force field constants by W. J. Balci and George.¹⁸⁰ An initial

SCF/STO-3G calculations of the vibrational properties of C_{60} and other symmetric carbon cages have been published by Disch and Schulman,¹⁸¹ Schulman et al.¹⁸² have applied the *ab initio* and AM1 methods to fullerene-24 and fullerene-60 in order to obtain heats of formation, vibrational frequencies, and ionization energies. Coulombeau and Rassat have considered the vibrations of several fullerenes up to fullerene-120.¹⁸³ They have also discussed hydrofullerenes.¹⁸⁴ In addition to calculating the rotational properties on the basis of icosahedral symmetry analysis,¹⁸⁴ Weeks and Harter have carried out a normal mode study on the basis of a classical spring/mass model.¹⁸⁵ They have also discussed the rovibrational properties of fullerene-60.¹⁸⁵⁻¹⁸⁹ Stanton and Newton¹⁹⁰ extended and revised earlier MNDO studies giving detailed information on the normal modes. They have derived group theory invariance theorems for vibrational analysis and have discussed the A_u vibration which essentially consists of rotary oscillations of the pentagonal rings. Cyvin et al.¹⁹¹ used a 5-parameter force field to calculate the frequencies of the four IR active and 10 Raman-active modes; and Brendsdal et al.¹⁹² have considered approximate methods in order to determine all 46 vibrational frequencies. Brendsdal¹⁹³ has discussed the symmetry coordinates.

Slanina et al. have carried out a harmonic vibrational analysis within the AM1 method for fullerene-60 and also fullerene-70.¹⁹⁴ The study has been extended to include consideration of structural, energetic, and thermodynamic properties of both species using MMP2 and MNDO methods.¹⁹⁵⁻¹⁹⁷ Bakowies and Thiel^{198,199} have used the MNDO approach to calculate the IR spectra of a whole range of fullerenes from C_{24} – C_{240} . For C_{70} they deduce that one vibrational band should be significantly more intense than the rest, see section X.

Heymann has discussed the possibility that He may be trapped in a fullerene-60 cage.²⁰⁰ Calculations have been made of the spectroscopic properties of various intracage complexes by Ballester et al.²⁰¹ assuming the central atom is trapped in a polarizable uniform (spherical) dielectric cage. Kroto and Jura²⁰² have discussed the importance of charge-transfer processes in the spectra of neutral and ionic fullerene intra- as well as extracage (van der Waals) complexes. For the ions the energy is just the difference between the ionization potentials of the C_{60} cage and the encapsulated species. Van der Waals complexes such as $C_{60}H^+$ are likely to be particularly important (section XI). Rosen and Waestberg have calculated the electronic structure of $C_{60}La$ (and C_{60}) obtaining ionization energies and electron affinities for the neutral and ionic species within the local-density approximation.^{203,204} Saito²⁰⁵ has also used the local density approximation to calculate the electronic properties of $C_{60}M$ ($M = K, O, Cl$).

Theoretical calculations have been carried out on fullerene-60 derivatives such as hydrofullerenes by Coulombeau and Rassat¹⁸⁴ and by Scuseria²⁰⁶ who has also considered the perfluorofullerene, $C_{60}F_{60}$. Crystal packing considerations for spheroidal molecules including fullerene-60, have been discussed by Williams.²⁰⁷

Several papers have focused on the likely electrical and/or magnetic properties of the fullerenes in particular fullerene-60. Elser and Haddon^{208,209} using HMO

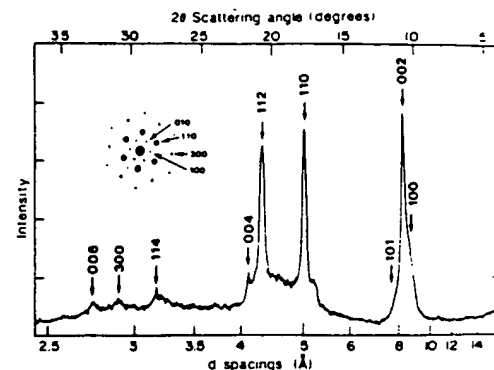


Figure 24. X-ray diffraction pattern of a microcrystalline powder of fullerene-60 obtained by Krätschmer, Lamb, Fostiropoulos, and Huffman.⁴ Inset (upper left) is a single-crystal electron diffraction pattern (shown in more detail in Figure 25) indexed with Miller indices compatible with the X-ray pattern. This pattern provided unequivocal evidence that the C_{60} species they had isolated was a round ball 10 Å in diameter in perfect agreement with expectation for buckminsterfullerene (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

and London theory, calculated the ring current magnetic susceptibility and concluded that the shielding should be vanishingly small (less than 1 ppm) due to cancellation of the diamagnetic and paramagnetic contributions. They concluded that fullerene-60 should not show normal aromatic behavior. Studies by Fowler, Lazzeretti, and Zanasi²¹⁰ and Pauling²¹¹ have suggested however that the diamagnetic term has been underestimated. From large scale *ab initio*, coupled Hartree-Fock calculations (involving all electrons) of the polarizability and magnetizability of C_{60} and C_{20}^{2+} , Fowler et al.²¹⁰ conclude that the shielding should be roughly the same as for related aromatic systems. Haddon and Elser²¹² have discussed their own results^{208,209} and reinterpreted those of Fowler et al.²¹⁰ and conclude that the latter study is consistent with a small delocalized susceptibility. Schmalz²¹³ has argued that the Fowler et al.²¹⁰ interpretation is correct. The NMR study of Taylor et al.⁶ yielded a chemical shift for fullerene-60 which is fairly typical for an aromatic species. Fowler et al.²¹⁴ have extended their approach to the calculation of the shifts in fullerene-70, obtaining results consistent with observation and confirming the line assignments made by Taylor et al.⁶ This problem is further discussed in section X.

IX. The Isolation, Separation, and Structural Characterization of Fullerenes-60 and -70

Almost five years, to the day, since the special behavior of the C_{60} signal was recognized (Figure 5) and the buckminsterfullerene proposal made,³ macroscopic samples were isolated and characterized. Krätschmer, Lamb, Fostiropoulos, and Huffman,⁴ in following up their earlier IR observations,^{5,74} discovered that at ca. 300–400 °C a solid material could be sublimed from the deposit obtained from arc-processed graphite. They found that this sublimate was soluble in benzene and could be crystallized. The X-ray and electron diffraction analyses (Figures 24 and 25) of the crystalline material so obtained (Figure 26) showed it consisted of

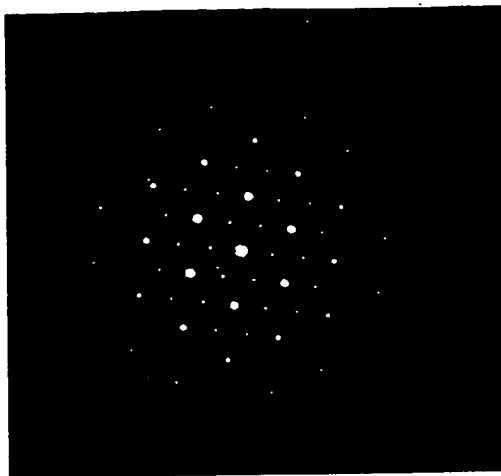


Figure 25. Single-crystal electron diffraction pattern of fullerene-60.⁴ Further details of indices are given in Figure 24 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

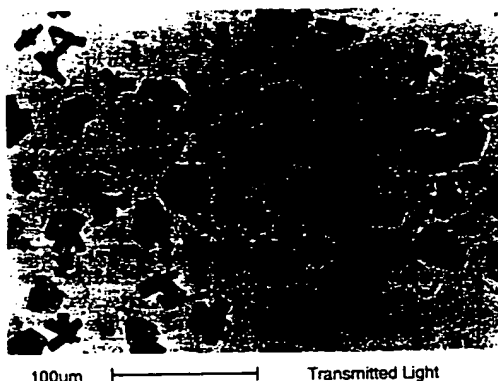


Figure 26. Transmission micrograph of crystals extracted by Krätschmer et al.⁴ from the deposit of arc-processed graphite. Thin platelets, rods and stars of hexagonal symmetry are observed (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

by ca. 3.1 Å (in graphite the interlayer distance is 3.4–3.5 Å). These authors also reported IR (Figure 27), UV/vis, and mass spectra of the extracted material. Bands of C₇₀ were present (weakly) in the IR spectrum and, in the UV/vis spectrum, some features of fullerene-60 were masked by those of fullerene-70. These results provided the first confirmation of the fullerene-60 structural proposal.

In a parallel and independent study of similarly arc-processed carbon, Taylor et al.⁶ had also shown that C₆₀ was present by FAB-sampled mass spectrometry and that a red soluble extract could be obtained by treating the carbon deposit directly with benzene. Taylor et al.⁶ processed the extract by the Soxhlet procedure and obtained a material which mass spectrometry showed to contain a range of fullerenes, C₆₀ and C₇₀ in particular (Figure 28). This material was chromatographed by using hexane/alumina, and C₆₀ and C₇₀ were thereby separated into a magenta and red fractions, respectively. ¹³C NMR measurements yielded a single line for C₆₀ (Figure 29a), providing definitive

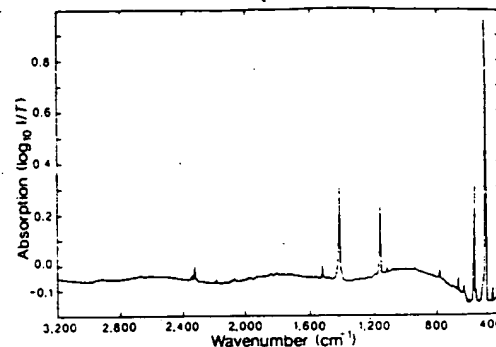


Figure 27. Infrared spectrum of fullerene-60 presented by Krätschmer et al.⁴ showing the four fundamentals in excellent agreement with expectation for the proposed fullerene-60 structure. Weaker features belong to fullerene-70 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

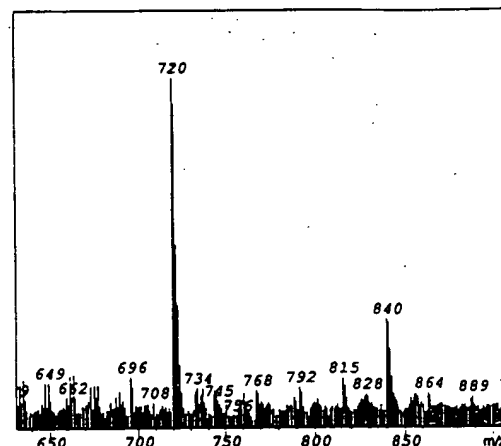


Figure 28. FAB-sampled mass spectrum, obtained by Taylor et al.⁶ of the soluble material extracted from arc-processed graphite. Apart from unequivocal evidence for C₆₀ and C₇₀ in the extract there is also evidence for other even-numbered carbon species, particularly C₆₈ and C₈₀ (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

proof that all 60 atoms are equivalent—a result totally commensurate with the buckminsterfullerene structure. There is of course the alternative solution that all the atoms are located on the perimeter of a monocyclic ring. This (explosively) unlikely possibility was eliminated by the NMR spectrum of C₇₀ which consisted of a set of five lines (Figure 29c) with a chemical shift pattern and relative intensities commensurate with the fullerene-70 structure (Figure 30b) first suggested by Heath et al.⁷ This result not only confirmed the fullerene 5/6-ring geodesic topology but also eliminated the possibility that the carbon atoms might be fluxional. Almost as important is the confirmation, by this result, of the existence of other members of the fullerene family.

X. Postbuckminsterfullerene Research—The First Results

Since the revelation that macroscopic samples of the fullerenes can be isolated and that they are soluble and

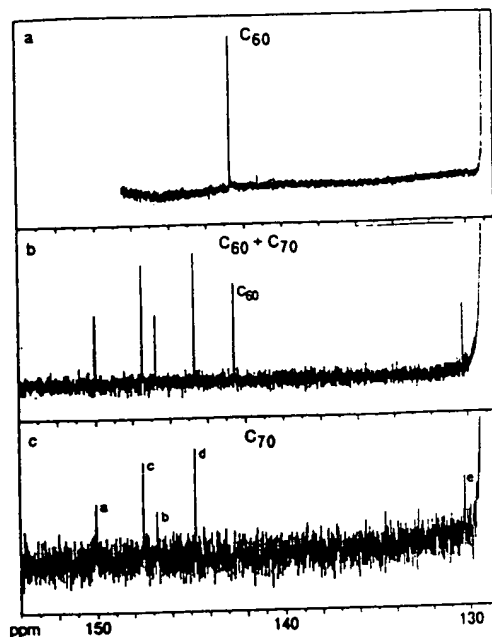


Figure 29. ^{13}C NMR spectra obtained from chromatographically purified samples (Taylor et al.⁶) of soluble material extracted from arc-processed graphite: (a) ^{13}C NMR spectrum of a purified sample exhibiting only a single resonance, (b) spectrum of a mixed sample, and (c) spectrum of a purified sample of C_{70} from which C_{60} has been eliminated. These spectra are consistent with the structures and assignments presented in Figure 20. The wing of the intense benzene solvent signal lies to the far right-hand side. This set of observations provided unequivocal evidence that the carbon atoms in C_{60} were indeed all equivalent in perfect agreement with expectation if the molecule were buckminsterfullerene (Figure 30). The five-line spectrum for C_{70} is also totally consistent with that expected for (D_{5h})fullerene-70 (Figure 30).⁷ This spectrum eliminated any lingering doubt there might have been that the C atoms were either fluxional or perhaps located on the perimeter of a monocyclic ring. It also provided evidence for the stability of other members of fullerene family⁷⁻⁹ (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

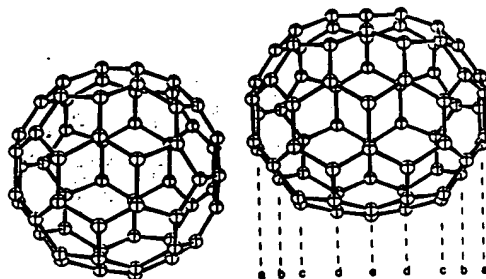


Figure 30. Schematic diagrams of fullerene-60 and fullerene-70 (based on diagrams of Slanina et al.¹⁹⁴). All sixty atoms in fullerene-60 are equivalent whereas fullerene-70 possesses five different types of carbon in the ratios 10:10:20:20:10 in the order a:b:c:d:e respectively as shown. Compare with the NMR spectrum shown in Figure 29.

chromatographically separable, it is now the turn of experimentalist to have a ball. Ajie et al.²¹⁵ and Hare et al.²¹⁴ have observed the UV/visible spectra of chro-

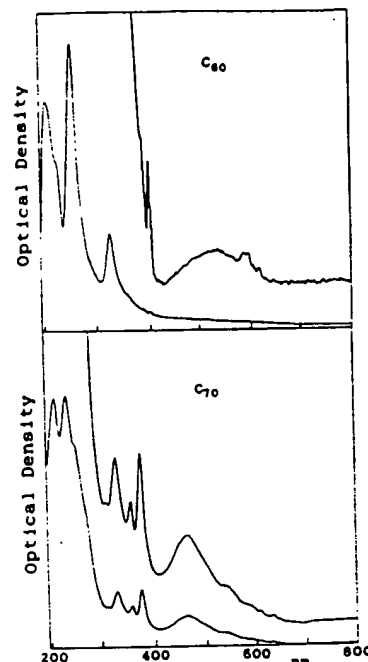


Figure 31. UV/vis spectra of chromatographically separated fullerene-60 and fullerene-70²¹⁵ in hexane solution (reprinted from ref 216; copyright 1991 Elsevier Science Publishers).

TABLE I. Properties of C_{60} Buckminsterfullerene

Vibrational Frequencies		
abs(obs) ^a	em(obs) ^b	calc. cm^{-1} ^c
528	527.1	472
577	570.3	618
1183	1169.1	1119
1429	1406.9	1434
X-ray Data ^d		
$r(\text{C}-\text{C}) = 1.388$ (9) Å six-six ring fusion		
$r(\text{C}-\text{C}) = 1.432$ (5) Å five-six ring fusion		
NMR Data ^e		
chemical shift (benzene soln) 142.68 ppm		
Electronic/Spectroscopic Data		
electron affinity ^f	2.6–2.8 eV	
ionization energy ^g	7.61 (0.02) eV	
UV/vis bands ^h	213, 257, 329 ($\epsilon_{\text{max}} = 135\,000, 175\,000, 51\,000$) 404 (w) 440–670 (brd) (max. 500, 540, 570, 600, 625) nm	

^aReference 4. ^bReference 218. ^cReference 191. ^dReference 222. ^eSee also Figures 24, 32, and 34. ^fSee Figure 28. ^gReference 6 (see also refs 215 and 228). ^hReference 99. ⁱReferences 101, 102, 239, and 240. ^jReference 216 (see also ref 215). ^kSee also Figure 31.

31). Reber et al.²¹⁷ have observed a luminescence spectrum. Frum et al.²¹⁸ have observed a most interesting IR emission spectrum from a hot gas-phase fullerene sample. The frequencies of the observed bands are given in Table I.

The availability of significant quantities of fullerenes has also opened up a Round Postbuckminsterfullerene Era of polycyclic aromatic chemistry. Haufler et al.²¹⁹ found that C_{60} can undergo Birch reduction to produce a white solid of formula $\text{C}_{60}\text{H}_{36}$. They point out that this formula is inconsistent with a cage hydrocarbon in

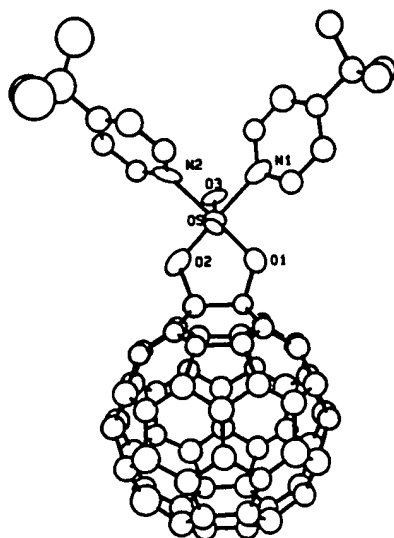


Figure 32. ORTEP drawing (50% ellipsoids) of the one-to-one C₆₀-osmium tetroxide adduct C₆₀(OsO₄)(4-*tert*-butylpyridine)₂, showing the relationship of the osmyl unit with the fullerene-60 carbon network²²² (reprinted from ref 222; copyright 1991 the American Association for the Advancement of Science).

which 12 isolated double bonds remain, possibly in the pentagonal rings. The reduction appears to be reversible. Evidence for the existence of a C₆₀U complex was obtained by the laser vaporization approach, used originally to detect C₆₀La.⁷ These authors also described the results of cyclic voltammetry measurements which indicated that C₆₀ has two reduction potentials. Similar measurements have been made by Allemand et al.²²⁰ who obtained a third potential. Their cyclic voltammetry measurements indicate that, curiously, fullerenes-60 and -70 appear to exhibit similar electrochemical behavior.

In one of the first attempts to introduce functional groups, Hawkins et al.²²¹ have found that they can form adducts of fullerene-60 with OsO₄(4-*tert*-butylpyridine) and its analogues. In a further study Hawkins et al.²²² have now obtained crystals of the osmium complex shown in Figure 32 and shown by X-ray analysis that rotation of the free C₆₀ spheroids in the solid phase has been eliminated by the attached group. This study has yielded the first carbon-carbon bond lengths for the fullerene cage (Table I). Arbogast et al.²²³ have observed fascinating photophysical behavior: fullerene-60 shows no fluorescence and efficiently catalyzes the formation of singlet oxygen. These authors observe a small S-T splitting of ca. 9 kcal/mol which is probably due to the large diameter of the molecule and the resulting small electron-electron repulsion energy. This together with the very low fluorescence rate and probably large spin-orbit interaction appears to account for the fact that intersystem crossing is a dominant process. Attention has been drawn to the fact that, due to their photophysical activity, care should be taken when working with fullerenes.

Hare et al.²²⁴ and Bethune et al.²²⁵ have made infrared measurements on chromatographically separated sam-

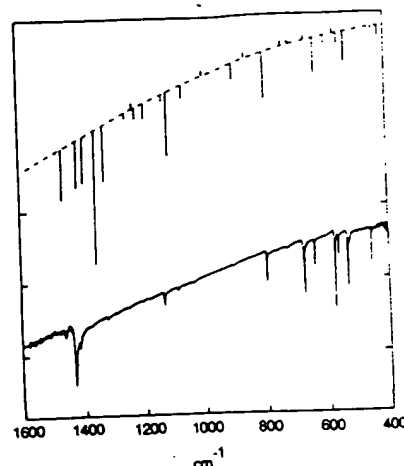


Figure 33. Infrared spectrum of chromatographically purified fullerene-70 obtained by Hare et al.²²⁴ and compared with the calculated spectrum of Bakowies and Thiel.^{196,199} The dashed curve is an estimated baseline. Note that the intensity of the very strong band calculated to lie near 1400 cm⁻¹ has been arbitrarily reduced by a factor of 3 relative to other features. Features calculated to be very weak are indicated by markers above the estimated baseline (reprinted from ref 224; copyright 1991 The Royal Society of Chemistry).

ene-70 together with the calculated spectrum of Bakowies and Thiel^{196,199} is presented in Figure 33. Bethune et al.²²⁶ and Dennis et al.²²⁷ have also made Raman measurements of fullerene-60 and -70. Liquid-phase NMR studies of unpurified fullerene mixtures by Johnson et al.²²⁸ confirmed the result of Taylor et al.⁶ (carried out on fully chromatographically purified samples) that the fullerene-60 resonance is a single line. Ajie et al.²¹⁵ have also confirmed the NMR measurements of a single line for fullerene-60 and five lines for fullerene-70; the former on a separated sample, the latter on a mixed fullerene-60/-70 sample. A 2D NMR analysis on fullerene-70 by Johnson et al.²²⁹ has unequivocally confirmed the assignments made previously by Taylor et al.⁶ shown in Figures 29c and 30b. Further refinements by Fowler et al.²¹⁴ of previous studies²¹⁰ predict fullerene-60 chemical shifts in excellent agreement with experiment (within 3 ppm). The study also includes estimates of the shifts for fullerene-70 so supporting further the pattern of line assignments given by Taylor et al.⁶ (Figures 29c and 30b). Tycko et al.²³⁰ and Yannoni et al.²³¹ have made solid-state NMR measurements down to 177 K where the motion is sufficiently slow for chemical shift tensor data to be obtained. Fullerene-60 rotates isotropically at 296 K and fullerene-70 rotates somewhat more anisotropically. Haddon et al.²³² have measured the magnetic susceptibility of solid samples of fullerenes and found it consistent with a molecule with a small ring current (see discussion in section VIII). Fowler²³³ notes that when this result is compared and contrasted with the NMR shift of fullerene-60⁶ it may imply ambivalent character when the question of the molecules "aromaticity" is considered.

Perhaps scanning tunneling microscopy (STM) offers more than any other a satisfying feeling of what the

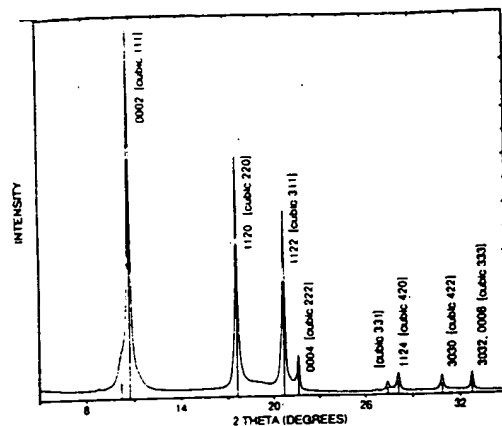


Figure 34. X-ray diffraction pattern obtained by MacKay et al.²²⁷ from a chromatographically purified fullerene-60 sample. The structure revealed is basically that of a strongly disordered stacking of a simple hexagonal close-packing, exactly as for elemental cobalt. The hexagonal unit cell refines to $a = 10.017 \pm 0.004$ Å and $c = 16.402 \pm 0.01$ and contains two C_{60} spheres. The spheres would be 1.68 g cm^{-3} . The lines can be indexed as shown and it will be noted that, because of the stacking disorder, only those reciprocal lattice rows parallel to c for which $-h + k = 3n$ are present. The c/a ratio of 1.637 is very close to the theoretical value of 1.633 and thus the pattern can also be indexed with respect to a face-centered cubic lattice (with $a = 14.186$ Å) (as of copper metal) with stacking disorder which removes the 200 and 400 reflections and which introduces a very weak line (the first) at a spacing of $a/(8/3)^{1/2}$ due to double diffraction from stacking faults. The intensity variation of the pattern as a whole corresponds to the transform of a sphere of radius 3.5 Å giving a first minimum in the region of $2\theta = 25^\circ$. Since the crystal is a mixture of FCC and HCP arrays, extracted crystalline material probably contains solvent molecules trapped in the faults.

et al.²³⁵ and Chen et al.²³⁶ have deposited fullerene monolayers on gold and studied them by STM. The spherical molecules tend to form mobile hexagonally packed arrays on a surface. Chen et al.²³⁶ observed local density variations on the surface of fullerene-60 which are highly suggestive of five- and six-membered rings.

The preliminary X-ray observations were made by Krätchmer et al.⁴ working with crystalline material consisting mainly of fullerene-60 with some fullerene-70 present. A recent X-ray diffraction image was obtained by MacKay et al.²²⁷ using chromatographically purified fullerene-60 (Figure 34). This image is commensurate with a completely random mix of HCP and FCC arrays of fullerene-60 molecules. Fleming et al.²³⁸ obtained purely FCC structured crystals from vacuum sublimed material. The implication is that interstitially trapped solvent probably stabilizes the mixed FCC/HCP crystals. It appears that fullerene-60 spheres are rotating in the lattice²³¹ and that when rotation ceases at low temperature the crystals are still disordered at the atomic level.^{221,222,238}

A most interesting study as far as theoretical chemistry is concerned is that of Lichtenberger et al.^{239,240} who measured the photoelectron spectrum of fullerene-60 on a surface and in the gas phase (Figure 35). The results are in good agreement with the theoretical (DV)-X α study of Hale¹⁶⁹ (Figure 23). The first IP of fullerene-60, 7.61 eV, is nicely consistent with the result obtained by Zimmerman et al.¹⁰¹ and McElvaney.¹⁰²

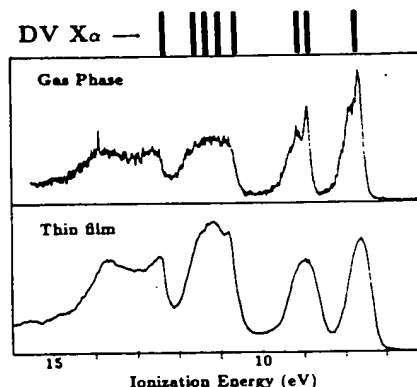


Figure 35. Gas phase (upper) and thin film (lower) He I valence photoelectron spectra of fullerene-60 obtained by Lichtenberger et al.^{239,240} The DV-X α results of Hale¹⁶⁹ (see Figure 23) which appear to be in good agreement with observation are indicated (reprinted from ref 239; copyright 1991 Elsevier Science Publishers).

Luffer and Schram²⁴¹ have made electron ionization mass spectrometric measurements on fullerene-60.

Several papers presented at a special symposium on the fullerenes (Nov 1990) have been collected together and published by Averback et al.²⁴² Some of the most important experimentally determined properties of fullerenes are presented in the Table I.

XI. Astrophysical Implications of C_{60}

Although low-temperature ion-molecule processes (Herbst and Klempner²⁴³ and Dalgarno and Black²⁴⁴) can account for most interstellar species, the long cyanopolyynes presented a problem. It was experiments which probed the possibility that carbon stars might be responsible for them^{31,32} which revealed the stability of fullerene-60.³ An important aspect of the experiments lay in the possibility of probing the conjecture of Douglas⁴⁰ that carbon chains might be responsible for the diffuse interstellar bands (DIBs). The DIBs are a set of interstellar optical absorption features of varying widths which have puzzled astronomers and spectroscopists since the mid-1930s. Herbig has published the definitive analysis of these features.^{245,246} Many possible contenders for the carrier have been suggested, however no generally accepted explanation exists so far. This is strange as the species responsible is clearly abundant, chemically bound (i.e. not atomic), and must be quite stable in order to survive in the hostile interstellar environment or, if destroyed, be very efficiently reformed. The types of carrier appear to be few in number and must have very large electronic absorption coefficients.

The possibility that C_{60} might be the widely distributed in the Universe and particularly in the outflows from carbon stars was suggested when the original discovery of its stability was made.³ It was also pointed out that the fullerene-60 surface might be an important site for the catalysis of interstellar reactions and perhaps it (or a derivative) might be responsible for such features as the DIBs. There is one key argument,^{50,55-58} associated with the proposal that fullerene analogues (ionized or un-ionized, complexed or otherwise) may be

the carriers has that all previous suggestions do not: fullerene-60 and its analogues are unique in that they appear to survive the violent processes which occur when the atomic components of a chaotic plasma condense to form particles. Various aspects of this original conjecture, particularly with regard to possible derivatives such as intracage complexes both ionized and neutral, have been discussed⁵⁵⁻⁵⁸ in general terms.

As far as the neutral fullerene-60 species in space is concerned, the negative results of searches based on the laboratory measurement⁵⁹ has been published by Snow and Seab²⁴⁷ and Sommerville and Bellis.²⁴⁸

The conditions in the ISM are such that a large fraction of any fullerene-60 molecules present is likely to be ionized and thus it has been pointed out that the spectra of ionized fullerenes such as C₆₀⁺ or fullerene analogues (such as the cage complexes C₆₀M⁺) might be responsible for some astrophysical features.^{55,57} Léger et al.²⁴⁹ and Joblin et al.²⁵⁰ have taken up the C₆₀⁺ proposal and considered it further.

Complexed species (section VIII) in the interstellar medium are particularly interesting as any C₆₀ present is likely to be ionized and probably have something stuck to its surface. As the DIBs exhibit features reminiscent of matrix spectra, the possibility that intracage complexes^{55,57,201-203} as well as the extracage complexes²⁰² might be responsible has been discussed. Heymann²⁰⁰ has considered the He intracage complexes and Bal-ester et al. other likely species containing O, Na, etc.²⁰¹ Kroto and Jura²⁰² draw particular attention to the fact that the charge transfer bands of the (C₆₀M)⁺ intracage complex and the van der Waals extracage complex (C₆₀)⁺M (M = alkali, alkaline earth, or other element) are likely to be very strong. Particularly interesting are possible relationships that charge-transfer transitions might have with the DIBs and perhaps also the strong unassigned 2170 Å absorption feature which has puzzled astronomers for over seven decades. Hoyle and Wickramasinghe²⁵¹ suggested that C₆₀ itself might explain this feature and further calculations relating to this possibility have been discussed by Braga et al.¹⁶⁷ Rablitzirov²⁵² has also discussed these possibilities. Wright²⁵³ has discussed the general optical/UV characteristics of fullerenes and concludes that the observed interstellar extinction is not consistent with the presence of significant quantities of spheroidal particles with graphite-like outer shells. In this respect the existence of the amorphous carbon surface layers surrounding the graphite cores of carbon microparticles may well be important.¹¹⁶ From the UV/vis spectra obtained so far^{4,215,216} it is clear that neutral fullerene-60 is not responsible for either the DIBs or the 2170 Å hump.

There are also some intriguing interstellar emission features in the IR, termed the unidentified infrared bands (UIBs), which have been assigned to PAH-like material by Duley and Williams,²⁵⁴ Léger and Puget,²⁵⁵ and Allamandola et al.²⁵⁶ The assignment rests largely on the reasonable correspondence between the astrophysical frequencies and those of polycyclic aromatic molecules which are usually used for fingerprint identification of large PAHs. Balm and Kroto²⁵⁷ have discussed the fact that, if the fullerene-60 concept is correct, PAH material in space is likely to be nonplanar. They point out that one feature, namely that at 11.3

The new results also offer possible new avenues of study as far as condensed carbonaceous matter in the cosmos is concerned. According to McKay et al.²⁵⁸ caged carbon clusters may offer a plausible explanation of some of the isotope anomalies observed in the elemental analysis of carbonaceous chondrites particularly the ²²Ne anomaly. Clayton²⁵⁹ has pointed out that condensation in the atmospheres of supernovae might explain the so-called Ne-E anomaly. McKay et al.²⁵⁸ have suggested that this observation might be explained by encapsulation of ²²Na in fullerene cages or icospiral embryos during the dust formation phases that follow supernova and nova outbursts. Subsequently, the decay of ²²Na yields an encapsulated ²²Ne atom. Zinner et al.²⁶⁰ have pointed out that isotope anomalies are only to be found in spheroidal carbon grains. So far the only evidence that C₆₀ might exist in space is an unconfirmed report by Anderson.²⁶¹

XII. Conclusions

It took some 15 or so years before the imaginative theoretical conjectures of Osawa and Yoshida^{3,14} and Bocharov and Gal'pern^{17,18} were realized in the discovery of the stability of the C₆₀ mass spectrometric signal³ in 1985. A further period of five years elapsed during which time many experimental measurements and theoretical studies were made. By-and-large the theoretical work (section VIII) substantiated the idea that buckminsterfullerene should be stable. As time elapsed the weight of circumstantial evidence grew and ultimately became convincing. The key observations include:

- (1) Detection of monometallic complexes indicated that atom encapsulation was feasible.^{7,96}
 - (2) Further cluster beam studies showed 60 to be a magic number whether the carbon species was positively or negatively charged or neutral.^{64,66,52}
 - (3) Reactivity studies showed the molecule to possess an inertness that was consistent with closure and the absence of dangling bonds.^{103,96}
 - (4) The pentagon isolation principle explained the observation of C₆₀ as the first magic number and C₇₀ as the second.^{8,9} Thus it was shown that the fullerene hypothesis rested on the observation of two magic numbers and not just one. Further refinement of the geodesic principle explained other observed magic numbers.^{8,9}
 - (5) Large fullerene networks were found to possess quasicrystalline structures and thus related giant concentric cage species¹⁰⁸ appeared to explain the infrastructure of the carbon microparticles observed by Iijima.^{109,110}
 - (6) Photoelectron measurements of Yang et al.⁹⁹ were also quite consistent with the fullerene conjecture.
- These and other studies (discussed in sections V-VII) thus had laid the background against which the critical infrared observation of Krätschmer et al.^{5,74} was made. They were led to make this observation by considering that some intriguing optical features observed in 1982 might be due to buckminsterfullerene. These observations were followed up by Krätschmer, Lamb, Fostiropoulos, and Huffman⁴ and Taylor et al.,⁶ and the results have revolutionized the field in that now the material can be made in quantity and the properties of

It is interesting to note that the motives for the experiments which serendipitously revealed the spontaneous creation and remarkable stability³ of C_{60} were astrophysical. Behind this goal lay a quest for an understanding of the curiously pivotal role that carbon plays in the origin of stars, planets, and biospheres. Behind the recent breakthrough of Krätschmer et al. in producing macroscopic amounts of fullerene-60, lay similar astrophysical ideas.⁴ It is fascinating to now ponder over whether buckminsterfullerene is distributed throughout space, and we have not recognized it, and that it may have been under our noses on earth, or at least played an important role in some very common environmental processes, since time immemorial.

The material is already exhibiting novel physical and chemical properties and there can be little doubt that an exciting field of chemistry and materials science, with many exciting applications has opened up. One of its most important properties is its ability to accept electrons. The low-lying LUMO causes it to be a soft electrophile.

It is perhaps worthwhile noting that C_{60} might have been detected in a sooting flame decades ago and that our present enlightenment has been long delayed. How serious this delay has been only time will tell; however, already fullerene chemistry is a vibrant field of study and the prospects for new materials with novel properties is most promising. Certainly, a New Round Postbuckminsterfullerene World of carbon chemistry appears to have been discovered, almost overnight. It should not be long before the molecule becomes a standard in textbooks; indeed construction procedures for fullerene-60 and giant fullerenes are to be found in the educational literature.^{12b,262}

Warning

The UCLA group has pointed out the importance of treating the material with great caution at this time when so little is known about it.²⁶³ Its ability to catalyze the formation of singlet oxygen and its novel chemical behavior inevitably suggest the possibility that the fullerenes might be carcinogenic. Particular care should be taken to ensure that the dust is not inhaled during preparation of the soot itself.

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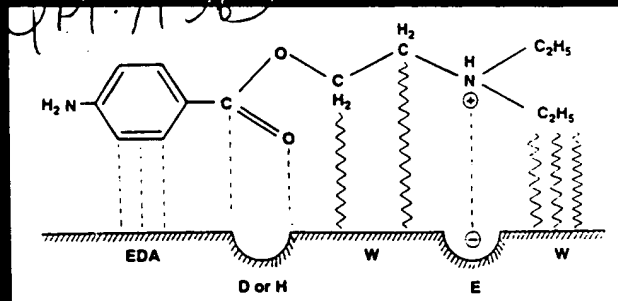
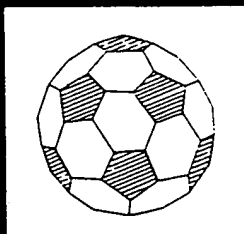
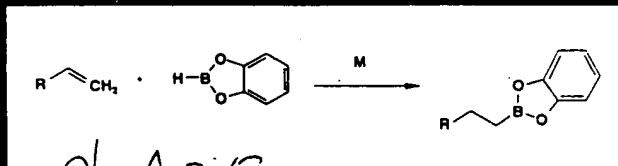
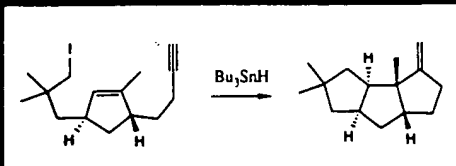
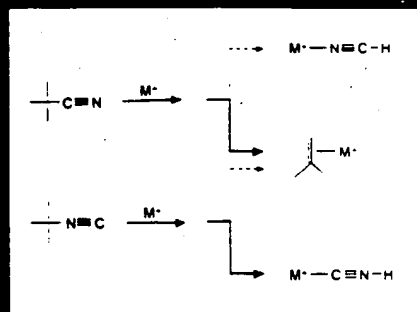
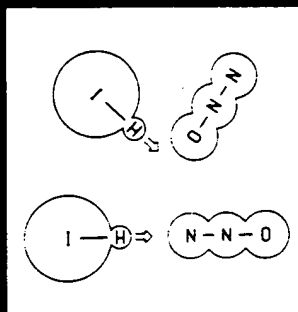
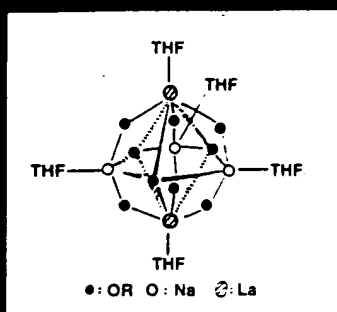
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CHEMICAL REVIEWS



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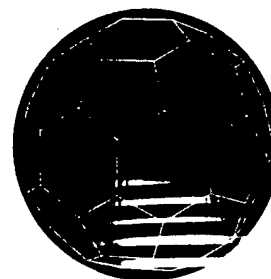
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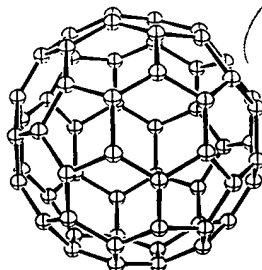
E3

The cover picture shows a section of a high-frequency oven used in a novel synthesis of fullerenes. The reaction zone (at approximately 2800 °C, the light is dimmed by the soot beginning to deposit) is depicted at the start of the fullerene production. The inductor, boron nitride insulation tube, quartz tube, and initial formation of smoke can be seen. More about the novel efficient synthetic method is reported by M. Jansen and G. Peters on page 223. The boom in fullerene chemistry continues. The third in a series of highlights on the important recent results (previous updates were published last year in the January and June issues) will appear in the next issue. An overview of the preparations, properties, and reactions of C_{60} is planned. This issue includes two highlights on silicon clusters including Si_{60} (p. 173), a communication on $He@C_{60}$ (p. 183), and, last but not least, an exciting account by H. Kroto on the start of the fullerene story (p. 111).



Review Articles

A "round organic chemistry" has burgeoned this last year following the development of an efficient means of producing fullerenes in 1989/1990. One of the protagonists in the fullerene story describes in a lively personal style how this fascinating new chemistry came about. In this thriller he points out that the discovery of C_{60} in 1985 did not result from an applications-oriented search but rather from basic research and scientific curiosity.



C_{60}

H. W. Kroto*

Angew. Chem.
Int. Ed. Engl. **1992, 31, 111**...129

C_{60} : Buckminsterfullerene, The Celestial Sphere that Fell to Earth

Almost atomic resolution is achieved today in techniques for studying monomolecular Langmuir films of amphiphilic molecules. Synchrotron X-ray sources providing well-collimated, high-intensity radiation make this possible. In this review the principles and methods used to study thin films are discussed. In these investigations, for instance, a strong influence from solute molecules or ions in the subphase on the crystallinity of the monomolecular layer was revealed: whereas α -glycine increases the crystallinity of a fluorocarbon monolayer, β -alanine decreases it. Possible explanations for the phenomena are also presented.

D. Jacquemain, S. G. Wolf, F. Leveiller,
M. Deutsch, K. Kjaer,* J. Als-Nielsen,*
M. Lahav,* L. Leiserowitz*

Angew. Chem.
Int. Ed. Engl. **1992, 31, 130**...152

Two-Dimensional Crystallography of
Amphiphilic Molecules at the Air-Water
Interface

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C₆₀: Buckminsterfullerene, The Celestial Sphere that Fell to Earth

By Harold W. Kroto*

In 1975–1978 the long-chained polyynylcyanides, HC₅N, HC₇N, and HC₉N were surprisingly discovered in the cold dark clouds of interstellar space by radioastronomy. The subsequent quest for their source indicated that they were being blown out of red giant, carbon stars. In 1985 carbon-cluster experiments aimed at simulating the chemistry in such stars confirmed these objects as likely sources. During these cluster studies a serendipitous discovery was made; a stable pure-carbon species, C₆₀, formed spontaneously in a chaotic plasma produced by a laser focused on a graphite target. A closed spheroidal cage structure was proposed for this molecule, which was to become the third well-characterized allotrope of carbon and was named buckminsterfullerene. It has taken five years to produce sufficient material to prove the correctness of this conjecture. There may be a timely object lesson in the fact that exciting new and strategically important fields of chemistry and materials science have been discovered overnight due to fundamental research, much of which was unable to attract financial support, and all of which was stimulated by a fascination with the role of carbon in space and stars. In this account, interesting aspects of this discovery, its origins, and its sequel are presented. The story has many facets, some of which relate to the way scientific discoveries are made.

Molecules with Unsaturated Carbon Bonds

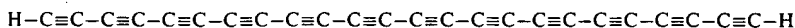
In the early 1970s, the chemistry of carbon in unsaturated configurations became the prime research focus for my group at the University of Sussex.^[1] We were interested in free unstable species and reaction intermediates containing C-S, C-P, C-Si, or even C-C multiple bonds. The work originated from an abortive attempt to produce thioformaldehyde (H₂C=S) by photolysis. However, we switched immediately to thermolytic activation after I heard a lecture in which Don Johnson (from the U.S. National Bureau of Standards in Washington, D.C.) described how he and Powell had made this compound^[2] by passing MeSSMe vapor through a quartz tube heated simply by a bunsen burner!

This approach worked beautifully; we produced numerous other new compounds containing the C=S moiety such as thioethanal and thioketene by thermolysis of specially synthesised precursors, and characterized them mainly by microwave and photoelectron spectroscopy.^[1] These sulfur species possessed a distinctive odor, and I for one have sympathy with the citizens of Freiburg who, according to Noller,^[3] forced Baumann and Fromm to abandon their work on these compounds. We gave up our work on seleno analogues for similar reasons after detecting seleno-propanal! After success with sulfur/carbon compounds we jumped, in the spirit of Mendeleev, to the next element in the second row of the periodic table, phosphorus. The first phosphaaalkenes, CH₂=PH and CH₂=PCl,^[4] were produced in 1976 in a joint project with John Nixon; several more followed.^[1] Simultaneously, Becker in Germany made PhP=C(*t*Bu)OSiMe₃.^[5] At this stage I envisaged a simple possible solution to the problem which had been on my mind

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since 1964, namely to ascertain whether derivatives of Gier's beautiful molecule $\text{HC}\equiv\text{P}^{[6]}$ could be made. I had been fascinated with $\text{HC}\equiv\text{P}$ since the day I arrived as a postdoc at the National Research Council (NRC) laboratory in Ottawa and heard Takeshi Oka (who was then also an NRC postdoc) enthuse over a spectrum of this molecule which Kelvin Tyler (another NRC postdoc) had just obtained.^[7] It seemed to me that the chemistry of $\text{HC}\equiv\text{P}$ and its analogues must parallel that of the nitriles. Transition-metal complexes could probably be prepared, and cycloadditions to generate phosphorus-containing rings would be feasible.^[8, 9] The simple approach worked very well, and we produced the first phosphaacetylene derivative, $\text{CH}_3\text{C}\equiv\text{P}$,^[10] by thermolysis of EtPCl_2 (provided by R. Schmutzler). We followed this breakthrough with the syntheses of other $\text{XC}\equiv\text{P}$ species ($\text{X} = \text{Hal}, \text{Ph}, \text{N}\equiv\text{C}, \text{N}\equiv\text{C}-\text{C}\equiv\text{C}, \text{etc.}^{[11]}$). It is most satisfying that, as I had originally conjectured in 1964, the phosphalkynes (and the phosphalkenes) have subsequently been exploited by ourselves and other groups as synthetic building blocks.

In parallel with our studies of compounds made up of second-row elements and carbon we probed molecules containing chains with $\text{C}-\text{C}$ multiple bonds. My fascination with such chains developed very early on in a study of the peculiar molecule, carbon suboxide $\text{O}=\text{C}=\text{C}=\text{O}$ (one subject of my Ph.D. work at Sheffield in the early 1960s with my supervisor Richard Dixon). This stimulated my curiosity in extended carbon chains and the unusual flexibility which they often exhibited; a preoccupation with such molecules has continued to this day. When I flash-photolyzed C_3O_2 a year or two later at the NRC, I ended up with a cell full of black soot and a magnificent spectrum of the C_3 molecule, whose enigmatic patterns had finally been deciphered by Gausset et al.^[11] Almost everything about these carbon chains seemed idiosyncratic, and I stored such observations up for the future. These memories were reawakened in the early 1970s by David Walton's work on polyynes at the University of Sussex. David had developed elegant methods for synthesizing long-chain polyynes, based upon silyl-protection techniques which he pioneered in acetylene chemistry.^[12-14] He and his students had made the parent 24 carbon-atom species in minute quantities in solution and



even a 32 carbon-atom (silyl-protected) polyyne.^[13] These chains were precisely what was needed for a study of vibra-

tion-rotation dynamics—a topic which had attracted my interest. In my mind they conjured up an image of a microscopic quantum-mechanical cheerleader tossing a very bendy bamboo baton high into the air—and then attempting to catch the violently flexing and turning baton as it descended. The obvious first compound for microwave study was the cyanopolyyne, HC_3N , because of its expected enormous dipole moment. Walton devised a synthetic route; Anthony Alexander, a "Chemistry by Thesis" student (editorial comment: for an explanation see the acknowledgements at the end of the review), successfully prepared it and measured its microwave spectrum in 1974.^[15] This was a wonderful achievement for an undergraduate and a very important one for me, since it was the first molecule to be characterized on our newly acquired microwave spectrometer.



Fig. 1. The dark clouds in Taurus from Barnards 1927 survey, *Atlas of Selected Regions of the Milky Way*, (Ed.: E. B. Frost, R. Calvert), Carnegie Institute, Washington, D.C., 1927. Heiles's Cloud 2 is in the left-hand bottom corner as indicated by coordinate markers.

At about this time spectacular advances were being made in molecular radioastronomy. The black clouds which are smeared across our Milky Way galaxy (Fig. 1) were found to possess long-hidden dark secrets. Townes and co-workers^[16] opened the Pandora's box in 1968 and revealed that

the clouds are full of identifiable molecules. Astronomers suddenly realized what a key role molecules played in the



Harold Kroto, born in 1939, studied in Sheffield from 1958 to 1964 and received his Ph.D. for his research in the electronic spectroscopy of free radicals with R. N. Dixon. After three years of postdoctoral research at the National Research Council in Ottawa and Bell Laboratories, he started his academic career in 1967 at the University of Sussex in Brighton, where he became full professor in 1985. The most recent distinction Kroto has received is a Royal Society Research Professorship (1991). Since 1990 he has been chairman of the editorial board of the *Chemical Society Reviews*. His research interests include the spectroscopy of unstable species, carbon and metal clusters and microparticles, as well as interstellar molecules and circumstellar dust. Graphic design is his other passion.

intimate gas dynamics involved in the birth of stars and planets. Apart from well-known species such as ammonia, water, and ethanol—enough for 10^{28} bottles of schnapps in Orion alone—Bill Klemperer ingeniously identified the HCO^+ ion (protonated CO)^[17] which had not previously been detected in the laboratory. Thus space served not only as a playground reserved for astronomers, but it now presented chemists with a novel piece of apparatus, indeed a colossal new spectroscopic sample cell, containing a plethora of exotic molecules in a wide range of physico-chemical environments.^[18] Shortly after Turner^[19] had detected HC_3N by microwave frequencies, I wrote to Takeshi Oka at the NRC; my group had recorded the analogous frequencies of HC_5N , and I wanted to search for the molecule in space. Takeshi and I had worked (1964–1966) in the same laboratory at the NRC during the golden years of that research organization.^[*] He replied saying that he was “very, very, very, very, very much interested”.

In November 1975 the search for radio waves of HC_5N (with Canadian astronomers Lorne Avery, Norm Broten, and John MacLeod) resulted in the successful detection of a signal from Sgr B₂, a giant cloud of molecules near the center of the galaxy.^[20] Although we had been hopeful, we were surprised by our discovery since it had seemed such a long shot. In 1975 molecules with more than three or four heavy (C, N, or O) atoms were assumed to be far too rare to be detectable. However, having found HC_5N in space, we thought that HC_7N might also be present. Walton devised a synthesis of HC_7N , and graduate student Colin Kirby managed the very difficult problem of making it and measuring its spectrum.^[21] By the time Colin (in England) finally succeeded in recording the vital frequency, we were actually working on the radio telescope, since our allotted observing session had already started. Colin telephoned my wife, who wrote the value on an envelope (Fig. 2 left). She then tele-

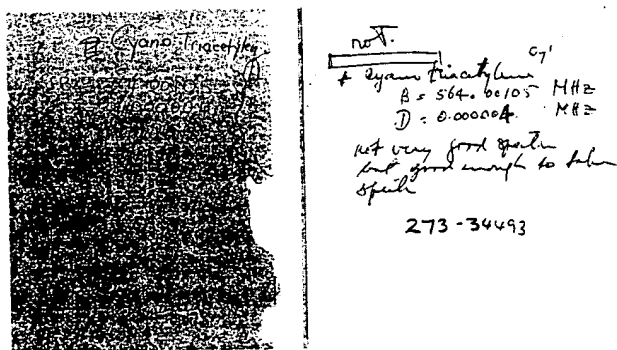


Fig. 2. The envelope (left) and intermediate note (right) with the precious experimental data from which the frequency of HC_7N in space was determined.

phoned Fokke Creutzberg, a friend in Ottawa, who also noted it carefully (Fig. 2 right) and transmitted it to us at the telescope site in Algonquin park (Fig. 3). The next few hours were high drama. We dashed out to the telescope and tuned the receiver to the predicted frequency range as Taurus

(Fig. 1) rose above the horizon (perfect timing). We tracked the extremely weak signals from the cold dark cloud throughout the evening. The computer drove the telescope and stored incoming data, but to our frustration we could not process the data on-line while the telescope was running. The system did, however, display individual ten-minute integrations, and as the run progressed we watched the oscilloscope for the slightest trace of the predicted signal in the receiver's central channel. During the course of these ten-minute snapshots, we gradually concluded that the central channel signal was possibly higher on the average than nearby ones. Desperate for even the faintest scent of success, we carried out a simple statistical analysis in order to determine whether the signal level of the channel was greater than the noise. As the night wore on we became more and more excited, convinced that the signal was significantly more often high than low; we could hardly wait for Taurus to set. By 1:00 a.m. we were too excited and impatient to wait any longer, and shortly before the cloud vanished completely, Avery stopped the run and processed the data. The moment when the trace in Figure 4 appeared on the oscilloscope was one of those that scientists dream about and which, at a stroke, compensate for all the hard work and the disappointments which are endemic in life. The circumstances of this discovery—the arrival of the value of the microwave fre-

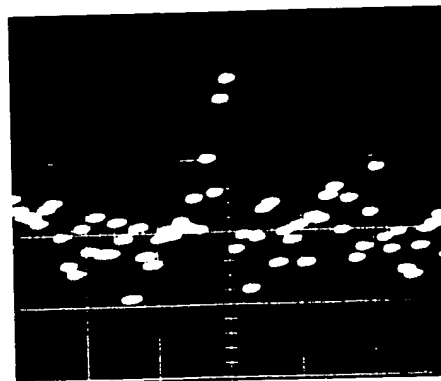


Fig. 4. The first oscilloscope trace of the radio signal emitted by interstellar HC_7N in Heiles's Cloud 2 in the constellation of Taurus (see the coordination markers in Fig. 1).

[*] Under the guidance of Gerhard Herzberg the NRC had become the Mecca for spectroscopists, and it was here that Cec Costain introduced me to the delights of microwave spectroscopy.

quency from the UK just in the nick of time, the gradual growth of the conviction that there might be a signal in that central channel of the receiver, and then finally the revelation that we (Fig. 5) had detected an enormous molecule in space^[22]—made for a truly cathartic scientific experience. (Modern on-line data processing would have diminished the experience). Obviously, the next candidate was HC_9N , but



Fig. 5. The team at the NRC laboratory just after the detection of HC_9N in space (from left): Avery, Oka, Broten, MacLeod, and Kroto.

its synthesis was a daunting task. Fortunately, Oka developed a beautifully simple extrapolation technique with which he predicted the radio frequencies of HC_9N . Almost unbelievably, we detected this molecule as well!^[23] Bell et al. later detected even HC_{11}N .^[24]

The Search for the Source of Carbon Chains in Space

It is not so obvious today, but in 1975–1978 such long-chain molecules were a totally new and unexpected component of the interstellar medium. How such species came to be present was not at all clear. I felt that it was not sufficient just to have co-discovered them; I really wanted to solve the puzzle of how they got there in the first place, and indeed what they were doing there anyway. After all, everything in nature seems to have some role to play. The search for the source of these compounds became something of a preoccupation (even an obsession). By the early 1980s I was convinced that the ion–molecule reactions which Eric Herbst and Bill Klemperer,^[25] and Alex Dalgarno and John Black^[26] had devised, and which accounted beautifully for almost all other interstellar molecules, really could not explain the origins of chain molecules.^[1, 18] It gradually became clear to me that red giant, carbon stars must hold the key. Particularly interesting was the spectacular infrared object IRC+10216, discovered by Eric Becklin and his colleagues,^[27] which pumps vast quantities of chains and grains out into space. I wondered about this red giant and the fact that it was shrouded in grains and chains, which were formed at roughly the same time.^[1, 18] and whether “the long chains may be an intermediate form of carbon, between atoms and small molecules such as C, C_2 , and C_3 , which are well

known, and particles with high carbon content such as soot”.^[1] Perhaps some symbiotic chain/dust chemistry was involved.

The First Visit to Rice University (Easter 1984)

The foregoing account sets out the background for my thoughts about the role of carbon in space prior to my trip to Rice University in Texas during Easter 1984 to visit Bob Curl. Almost the first thing that Curl told me was that I should visit his colleague, Rick Smalley. He enthused over a very recent result obtained by Smalley and his co-workers, who had analyzed the spectrum of the SiC_2 and had shown the molecule not to be linear, as some might have expected, but triangular.^[28] (The analogous C_3 species is linear, although only just.^[11]) I visited Smalley's laboratory and saw the laser vaporization cluster-beam apparatus which he and his co-workers had recently developed. This powerful technique enabled the mass-spectrometric study of stable clusters formed in a helium-entrained plasma, produced by a pulsed laser focused on a solid target. In this particular experiment silicon carbide was vaporized and the electronic spectrum of SiC_2 observed.^[28] I was much impressed by the result but even more by the experimental technique.^[29] This method was clearly a major breakthrough in cluster science, since it made refractory clusters accessible for detailed study for the first time. I had already heard of it, but to see the apparatus in operation was quite fascinating. The result of the SiC_2 experiment was particularly interesting to me, because it was consistent with some unusual theoretical results for >Si=C< species^[30] obtained at Sussex in collaboration with John Murrell some years earlier. What excited me most, however, was the thought that by simply replacing silicon carbide with graphite, it should be possible to simulate the type of chemistry which takes place in the atmosphere of a carbon star and produce the long carbon chains. As the day wore on I became more and more convinced that the technique was perfect for this purpose and that evening discussed it with Curl. Because of his interest in microwave spectroscopy, he was immediately enthusiastic, and we made plans for a joint project in the hope that Smalley would also be interested. Perhaps we could detect chains with as many as 24–32 carbon atoms related to Walton's polyyynes or Hintonberger's equally amazing pure-carbon species (C_{33} etc.), which were detected by mass spectrometry in the early 1960s in a carbon arc.^[31] I dreamt that one day it might be possible to detect a chain molecule such as HC_{33}N (which is as long as the chains that Walton had made in a test tube) in space. Curl was particularly excited by the prospect that we could check out an interesting idea of the late Alec Douglas,^[32] namely, that carbon chains might be carriers of the famous Diffuse Interstellar Bands—a set of absorption features^[33] which have puzzled astronomers and spectroscopists for more than six decades. Because the project was not considered a priority by the cluster group at Rice University at that stage, it had to await a convenient slot in their program.

In the interim, a group at Exxon carried out the basic graphite-vaporization experiment. In the summer of that year (1984) they published a fascinating result: the discovery of a totally new family of carbon clusters $\text{C}_{30}\text{--C}_{190}$ ^[34]—

much larger species than those prepared by Walton et al.^[12-14] or observed by Hintenberger.^[31] This exciting discovery was peculiar because only even-numbered clusters were detected. It is important to note that at this juncture no specific cluster was perceived to be special. In August 1985 (almost 18 months after my visit) Curl telephoned to say that carbon experiments were at long last imminent. He asked whether I wanted to come to Houston to participate or if they should carry out the experiments and send the data to me. One thing was certain in my mind: I had not waited this long to have my experiments carried out by others in my absence; I wanted to do them myself and to direct the operation personally. Therefore I packed my bags and at my wife Marg's expense arrived at Rice University within days.

Second Visit to Rice University— The Discovery of C_{60}

Silicon and germanium cluster studies were on the Rice plate in August 1985 because of their implications for semiconductors. Such experiments were considered to be important because the results might have useful applications (!) The carbon project, on the other hand, was thought to have no possible application (other than for astronomy) and was to be completed quickly, causing as little delay to the semiconductor study as possible. Preliminary measurements on carbon had already been carried out, and the Exxon spectra had been reproduced; nothing untoward was noticed. As soon as I arrived (August 28th) I presented a lengthy informal seminar on everything I knew about carbon in space, stars, and soot. My experiments started on Sunday, September 1st, 1985. I worked in the laboratory alongside two research students, Jim Heath and Sean O'Brien—an exhilarating experience; Yuan Liu was also involved. We toiled late into the night, varying the clustering conditions and monitoring the reactions of the carbon clusters with hydrogen, oxygen, and ammonia—gases which I thought would give rise to polyynylcyanides and other chain molecules. They did! The experiments thus immediately confirmed that the chemistry in red giant stars could be responsible for interstellar carbon chains. Curl and Smalley paid frequent visits to the laborato-

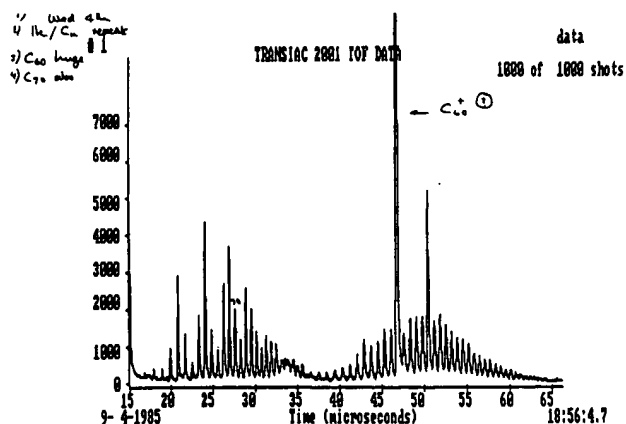


Fig. 6. Annotated time-of-flight (TOF) mass spectrum of carbon clusters produced on Wednesday, September 4th, 1985, the day on which the dominance of the C_{60} signal was first recorded (see also Fig. 7a).

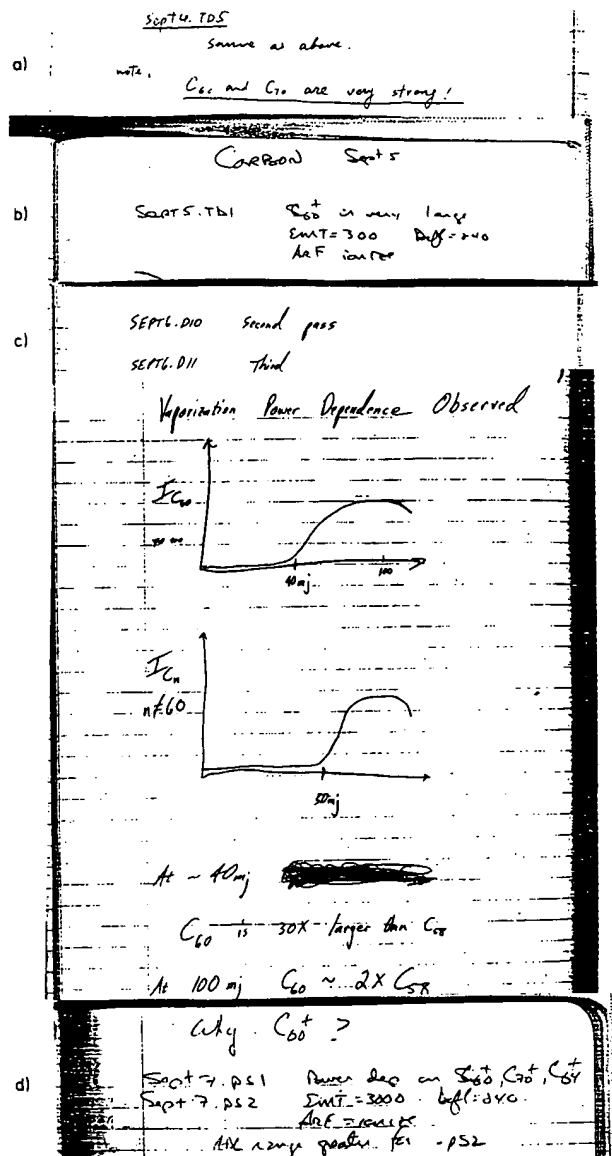


Fig. 7. Entries by Heath, Liu, and O'Brien in the Cluster Laboratory Notebook from the period September 4–7, 1985 when key experiments were carried out at Rice University. a) September 4th: First recorded note that C_{60} and C_{70} were very strong (see also Fig. 6). b) September 5th: C_{60} signal again very strong. c) September 6th: Record of first experiments which specifically aimed at optimization of the conditions for production of a dominant C_{60} signal (" C_{60} is 30 × larger than C_{58} .") d) September 7th: Further power-dependence studies.

ry. As the experiments progressed it gradually became clear that something quite remarkable was taking place: As we varied the conditions from one run to the next, we noticed that a peak at 720 amu^[*] (corresponding to a C_{60} species) behaved in a most peculiar fashion. Sometimes it was completely off-scale; at other times it was quite unassuming. The spectrum recorded on Wednesday, September 4th, 1985 was astounding (Fig. 6). Our reactions were noted in the laboratory record book (Fig. 7a), and I annotated my copy of the printout (Fig. 6). From that point onwards the idiosyncratic behavior of this peak was followed very, very closely (Fig. 7b). When this result appeared, the carbon project—

[*] Editorial note: amu = atomic mass unit. According to *Quantities, Units and Symbols in Physical Chemistry* (Ed.: Int. Union of Pure and Applied Chemistry), Blackwell, Oxford, 1989 (Chapter 2.10), amu is the symbol for the unified atomic mass unit m_u and the unit u. In this review the unit amu which is still encountered frequently is used.

for the first time—engendered general interest, and by mutual agreement continuation of the semiconductor program was delayed so that we could concentrate on the remarkable phenomenon which we had uncovered. As the weekend approached our actions, thoughts, and conversations turned more and more to the phenomenon. What might this special “wadge” of carbon be? Smalley had never come across this British term for a cluster and liked it so much that he started to refer to C_{60} as the “Mother Wadge”; the omnipresence of the cluster led me to call it the “Godwadge”. On Friday, September 6 during a group meeting, Curl suggested that we should concentrate on identifying the conditions under which the 720 amu peak was most prominent. O’Brien and Heath agreed to work shifts during the weekend. Experiments aimed specifically at optimizing the signal were carried out that same evening, and conditions were immediately found under which C_{60} peak was 30 times stronger than the adjacent C_{58} signal (Fig. 7c). After further optimization (Fig. 7d) the striking spectrum (Fig. 8) was finally obtained. C_{70} is also prominent!

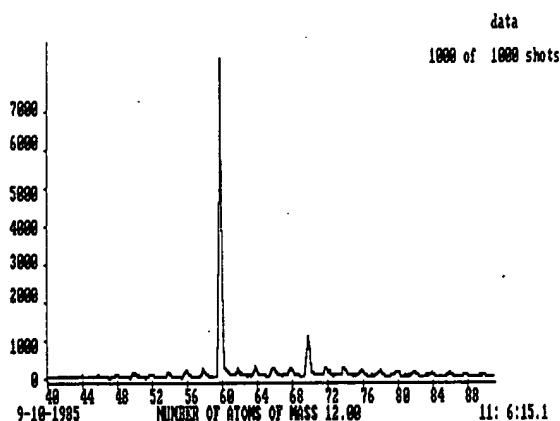


Fig. 8. TOF mass spectrum of carbon clusters under the optimum conditions for the observation of a dominant C_{60} signal.

The Structure of C_{60} (?)

What on earth could C_{60} (?) be? In the days following our discovery of C_{60} (Fig. 6), the signal began gradually to dominate our results as well as our thoughts and conversation. The quest for a structure which could account for this precocious wadge of carbon led to numerous, synergistic [Editorial comment: R. Buckminster Fuller's architectural constructions were based on a vectoral geometry which he called energetic—synergetic geometry. This was founded on a natural philosophy, according to which nature constructs systems of forces such that the maximal strength can be obtained from the minimum effort in construction.] discussions among all five members of the team during those days. The deliberations were particularly intense on Monday, September 9th. As this day wore on and all the ideas which had surfaced during the period were assessed and reassessed, a consensus grew that C_{60} might be some sort of spheroid. One possibility we considered was that the laser had blasted flakes of hexagonal carbon from the graphite surface, and that these hot graphite-like networks had somehow wrapped

themselves up into closed cages, thus eliminating the dangling edge bonds and making the cage unreactive. This idea had instant appeal for all. For me this concept brought back vivid memories of Buckminster Fuller's geodesic dome at EXPO '67 in Montreal (Figs. 9 and 10). I had actually

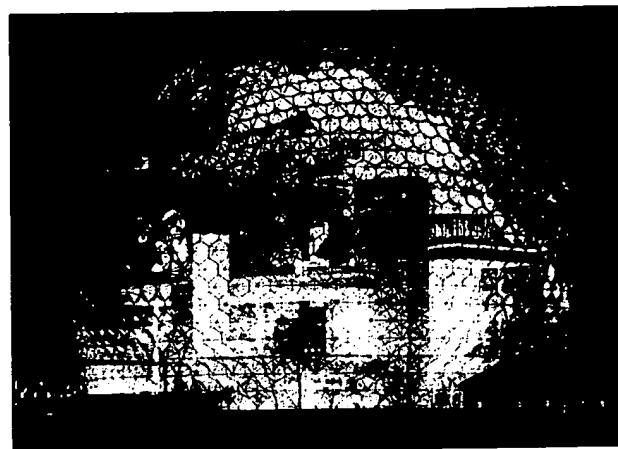


Fig. 9. Photograph (by Michel Proulx) of the geodesic dome designed by Buckminster Fuller for the U.S. exhibit at EXPO '67 in Montreal (taken from *Graphis* 1967, 132 379). One of the pentagons necessary for closure is discernable in this photograph.

been inside this remarkable structure at that time and remembered pushing my small son in his pram along the ramps and up the escalators, high up among the exhibition stands and close to the delicate network of struts from which the edifice was primarily constructed. This experience had left an image in my mind which could never be erased. I had collected numerous photographs of the dome from magazines over

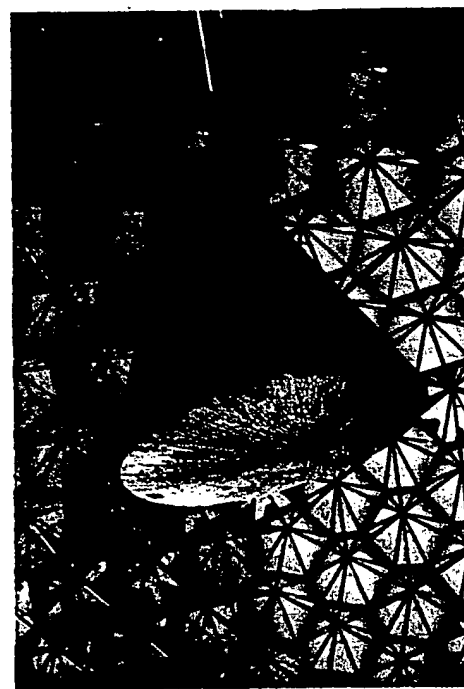


Fig. 10. Photograph (by Robin Whyman) of the inside of the EXPO '67 dome in Montreal. One of the pentagons necessary for closure is clearly visible in the middle section, as is the way in which the strut lengths have been adjusted to achieve a smooth round shape.

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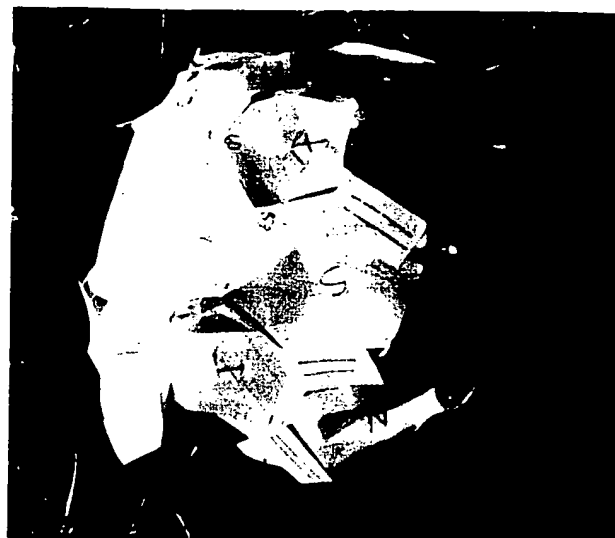
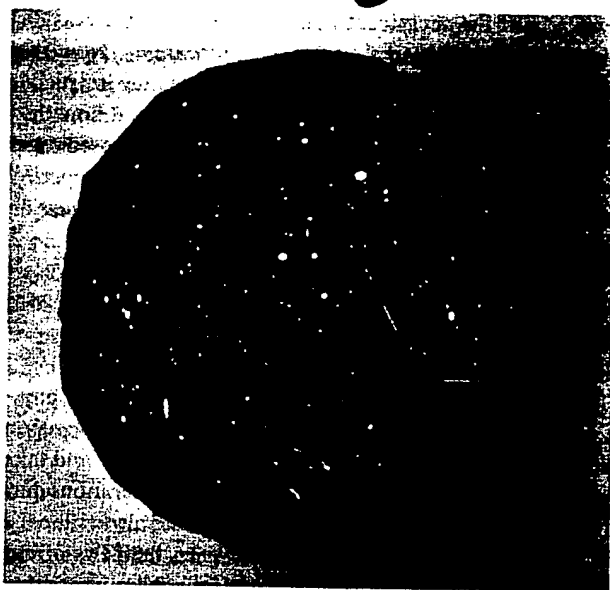


Fig. 11. The two cardboard polyhedra which played key roles in our search for the structure of C_{60} (see text). Left) stardome map of the sky (Buckminster Fuller patented icosahedral and other polyhedral world-map projections); right) Smalley's model with 60 vertices and 12 pentagonal and 20 hexagonal faces.

the years from Life, Paris Match, and Graphis. Particularly striking were those in my favorite graphic art and design magazine, Graphis, to which I had subscribed since my university days. As I remembered it, the Graphis pictures (Fig. 9) showed that the dome consisted of a plethora of hexagonally interconnected struts. Indeed, the dome had actually initiated my interest in some of Buckminster Fuller's other projects; I had even been in the process of writing to him with a view to working with him on the organized growth of massive urban structures. However, I did not pursue this, because I was offered a permanent academic position at Sussex at just that time.

As far as C_{60} was concerned, I wondered whether Buckminster Fuller's domes might provide some clue. Smalley also strongly favored some sort of spheroidal structure and suggested that we borrow a book from the Rice University library. We obtained a book by Marks^[35] in which geodesic domes of all kinds were described. In addition I had one or two other structural proposals which intrigued me: One was a four-deck model 6:24:24:6 (two coronene-like sheets sandwiched between two benzenoid ones) with a roughly spheroidal shape. It contained 60 atoms, and its symmetry suggested that the dangling bonds might be somewhat deactivated. However, I really could see no reason why this species would be as unreactive as C_{60} appeared to be; a closed-cage solution would certainly be more stable. A second image came to mind several times, most vividly on this particular Monday. This was of a polyhedral cardboard stardome (Fig. 11 left) which I had constructed many years before when my children were young. This map of the stars in the sky was tucked away in a cardboard box (that universal quantum of storage) downstairs in my home far away in England. I itched to get my hands on it and even described its features to Curl at lunch time. I remembered cutting out not only hexagons but also pentagons. I wondered whether I should telephone my wife to ask her to count the vertices in order to ascertain whether, as I half-suspected, they totaled sixty.

The Mexican Restaurant

I was due to return to the UK the next day, so that evening (Monday, September 9th) I thought we should celebrate our extraordinary discovery. I invited the group out to dinner at what had become our favorite Mexican restaurant. During the meal the conversation was naturally dominated by C_{60} (?). We again considered all the ideas which had come up in our deliberations during the days that had passed since the signal had first been noticed. We agreed unanimously on a *closed cage* structure. We talked about Buckminster Fuller's domes, Smalley, about chicken-wire cages, and I reiterated the essentials of the stardome—its spheroidal shape, hexagonal faces, and, in particular, the pentagonal faces. Smalley expressed an interest. After the meal other members of the group went home; I returned to the laboratory in order to study the Marks' book on Buckminster Fuller, but I could not find it. I again considered telephoning home about the number of vertices in the stardome. But it was now far too late since it was well after midnight in the UK.

Very early the next morning Curl telephoned to say that Smalley had experimented with paper models based on the stardome characteristics I had mentioned the previous day. Smalley had come up with something bigger than anything he (Curl) had ever been involved with before. When I got to the laboratory and saw the paper model (Fig. 11 right) which Smalley had constructed during the night I was ecstatic and overtaken by its beauty. It seemed identical to the stardome as I remembered it, and I was quietly pleased that my conjecture had been right all along. Heath and his wife Carmen had also experimented with a geodesic structure modeled out of jelly beans and toothpicks; it was not quite so convincing.^[36]

In summary, the quest for a rational explanation of the dominant line in the mass spectrum had reached a climax on Monday, September 9th. Ideas were suggested, refined, or critized in earnest throughout that final day. Buckminster Fuller's domes were invoked, Marks' book was consulted, and the stardome's pentagonal faces introduced at midday

and again in the evening; Smalley and the Heaths experimented further with models during the night after our meal. All this took place in a matter of hours, leaving no time for anything important—other than perhaps Marks' book—to "slip through the cracks".^[37] It was most satisfying that synergistic (a Fullerism) teamwork had been involved in the experimental observation as well as in the positing of the structure.

I delayed my flight home for one extra day (until Wednesday, September 11th) in order to help to write the publication. At one point Heath was sitting at Smalley's desk when the telephone rang. A mathematician, whom Smalley had consulted earlier to ask about the structure, informed Heath, "Tell Rick—it's a soccerball!" Almost unbelievably, until that moment, none of us had realized that the C_{60} structure we were proposing had the same symmetry as the modern soccer-(USA) or football (rest of the world). I do not know how I could have been so blind—my only (feeble) excuse was that the modern football was introduced after I ended my serious soccer-playing days. The other members of the team could be excused, since a structure related to the American football really was an unlikely contender, at least at that stage. We immediately purchased a real football and our five-a-side team posed for a photograph (Fig. 12). I also



Fig. 12. The five-a-side Rice/Sussex football team (from left): O'Brien, Smalley, Curl, Kroto, and Heath.

photographed Smalley's paper ball (Fig. 11 right), but when I queried the whereabouts of the Heath model in order to photograph it for posterity, I was informed that it no longer existed because Mary-Joe (another Rice graduate student) had eaten it. So all tangible record of a truly remarkable edifice was lost for all time.

Since the geodesic dome concepts had played such an important part in helping us to arrive at the solution (at least as far as I was concerned), I suggested that we name the compound buckminsterfullerene. Smalley and Curl fortunately agreed, accepting that though the name was long, it did indeed roll smoothly off the tongue. Thus we avoided the fearful international conflict over terminology which would have raged had we named it after a certain well-known ball game. Smalley could not resist putting some alternative suggestions for names at the end of the publication. The name

engendered the occasional mild criticism^[38] which was dispatched with a little help from Shakespeare.^[39] Now that some time has passed, it is satisfying to note how instructive (about geodesy) others have found the name and how flexible it has turned out to be. The whole family of closed cages can be appropriately named—fullerenes.^[40] The paper^[41] was dispatched by Federal Express to the journal *Nature* on the afternoon of Wednesday, September 11th, 1985.

Five Long Years in the Desert

The ten-hour nonstop flight home to England was a physical and psychological high for me. My first action upon entering the house was to open the cardboard box and take out the stardome which had influenced my deliberations during the search for the structure of C_{60} . It had always looked beautiful; now it positively glowed. When the news of our result spread, Martyn Poliakoff at Nottingham wrote that his friend, David Jones, had already thought of hollow carbon cages. In 1966 Jones had written a delightful article under the pseudonym Daedalus in the journal *New Scientist*^[42, 43] in which he had suggested that the high-temperature process in the production of graphite might be modified to generate graphite balloons. This was a typical example of the presciently "crazy" ideas of Jones. I thus learned about the Euler principle, which says that 12 pentagons are needed to close a network and that hexagons alone just will not do. I was introduced to D'Arcy Thompson's elegant book^[44] and learned that one could close an even-numbered carbon cage with any number of hexagons (except one, I subsequently learned) provided 12 pentagons were included in the network. The beautiful Aulonia (Fig. 13 photograph from Tibor Tarnai) already knew more than we about these simple (pentagonal) facets of (its) life. This was all fun and truly

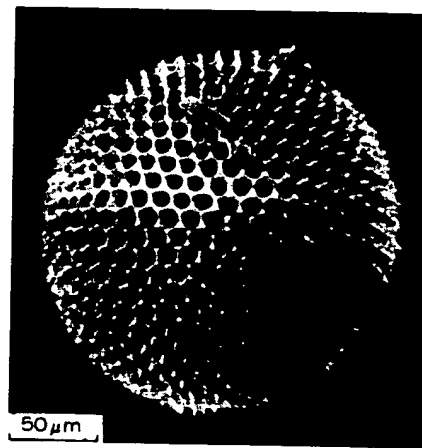


Fig. 13. A siliceous sea creature, *Aulonia hexagona*, appears at first glance to possess a skeleton composed completely of hexagons. Pentagonal structural elements are discernable, however (photograph supplied by Tibor Tarnai).

fascinating, because it became clear that there might even be other (even-numbered) carbon cages—there were certainly other (even-numbered) peaks (Fig. 6), in particular C_{70} . O'Brien and Smalley reached the same conclusions independently. Particularly important were a series of reactivity ex-

periments carried out by O'Brien, which showed that all the even-numbered carbon species were totally unreactive, a result neatly commensurate with closed structures for all the even-numbered cages.^[45]

I met David Jones, a most fascinating individual, who epitomizes so much of what the spirit of science should be about. We also learned that Osawa and Yoshida had already thought of C_{60} in 1970 and had even suggested that it might be superaromatic.^[46, 47] In 1973 Bochvar and Gal'pern^[48] also published a theoretical paper on the molecule. Thus it transpired that although there were some most imaginative scientists around, few—other than Orville Chapman at the University of California at Los Angeles (UCLA)^[49]—had noticed these pioneering flights of imagination.

Circumstantial Evidence for the Identity of the "Third Man"

The first question stimulated by the realization that we might have found a "third form of carbon" with a hollow, cage structure was obvious: is it possible to trap an atom inside the cage? My early Sheffield background led me to wonder whether iron might form an intriguing ferrocene-like analogue. The day I left, Heath tried to encapsulate iron without success, but the next day he succeeded in detecting a stable $C_{60}La$ complex.^[50] This experiment provided the first convincing piece of evidence to support our proposal of the cage structure. Then began what was to become a truly exhausting schedule for me: Every four to six weeks I flew to Houston, and after two to three weeks' work with the group at Rice I returned to the UK and my commitments in Sussex. As soon as I arrived in Houston I would present a group seminar based on ideas which I had developed while in the UK. This schedule continued until April 1987. From the outset the joint Rice/Sussex follow-up program had two clear objectives. First, to make enough C_{60} to prove beyond doubt that our structure was correct and second, to measure the optical spectrum of C_{60} which we had surmised might in some way be responsible for the Diffuse Interstellar Bands.^[41] These astronomical features had of course been partly responsible for the carbon-cluster experiment in the first place. These goals were all-consuming and we often talked about "the little yellow (Smalley's guess) or pink (my guess) vial" of C_{60} .

During the late 70s and early 80s I felt that it was simply not enough just to detect the carbon chains; the source must be tracked down. This obsession with the source led ultimately to the discovery of C_{60} . After 1985 I developed a similar attitude to C_{60} . Our discovery of a species which probably had a truncated icosahedral structure was "not enough", and as months and then years passed, confirmation of the structure and its identification in space also became somewhat of an obsession. We (the Rice group and myself) were convinced from the outset that our proposed structure was correct; surely it was too beautiful and perfect to be wrong. However, if for once aesthetics were misleading us, it would be much better if we proved our model wrong ourselves. It is certainly fair to say that the proposed structure was greeted with scepticism by some, though many loved C_{60} and were convinced that we were right from the

start. During this period (1985–1990) I examined the problem independently at Sussex, as well as in collaboration with the Rice group, who also made independent studies. In time all these efforts resulted in a mass of convincing evidence in support of our proposal.

From the moment we discovered that C_{60} was stable I had one all-consuming dream: I wanted to solve the molecule's structure by NMR spectroscopy. Because all 60 carbon atoms in buckminsterfullerene are equivalent, the ^{13}C NMR spectrum should consist of a single line. Proof of our radical proposal in such an exquisitely simple manner was to remain elusive for some five years; this goal was almost like a holy grail—far, far beyond reach. I was quite convinced that a clever young organic chemist would accomplish this task. I had one consoling thought, namely that we had been rather successful in the past with a series of molecules whose identifications were based on spectra consisting of single lines: Phosphaethene, $CH_2=PH$ (the first phosphaalkene made) had been assigned by its $J = 1 - 0$ microwave line^[1, 4] and HC_3N and also HC_7N had both been originally single radio-line detections in space.^[20, 22] Then there was, of course, the 720 amu peak in the mass spectrum of C_{60} .^[41] How fitting it would be to round it all off by *proving* by another *single* line that C_{60} was buckminsterfullerene.

C_{70} and the Fullerene Family

It is fair to say that I (and perhaps also my colleagues at Rice University) occasionally woke up in the middle of the night and wondered whether I should have to commit suicide if our idea turned out to be wrong. Had we stuck our necks out too far? These thoughts only lasted seconds. I would reassess all the evidence, realize that everything fitted, and go back to sleep convinced more than ever that C_{60} had to be a geodesic cage. Time passed, we made several advances,^[51, 52] and each time the cage concept clarified our observations. That was important. I remembered hearing Richard Feynman on BBC radio say that it seemed to him that if a radical new theory were right, it would allow the solution of previously unsolved puzzles. I quantified this: If an idea fitted 80–90% of the observations, it was almost certainly right; if more than 10–20% of the details had to be bent to fit, it was almost certainly wrong. Buckminsterfullerene was well up in the first category.

I remember vividly the day on which all my lingering doubts vanished. I was sitting at my desk thinking about the reasons why C_{60} might be stable. The missing piece of evidence in this personal jigsaw puzzle turned out to be so simple, it was almost child's play; indeed it evolved from my playing with molecular models of various conceivable cages. The solution was related to the C_{70} signal which always popped up prominently when C_{60} was strong. I used to call the two species "the Lone Ranger and Tonto"^[*] because

[*] The Lone Ranger und Tonto were a famous cowboy and Indian duo from the movies. As a child I saw them every week fighting crime in the Wild West. Bob Dylan immortalized them in the following blues text:
Well the Lone Ranger and Tonto
They are ridin' down the line
Fixin' ev'rybody's troubles
Ev'rybody's 'cept mine.
Somebody must a tol' 'em that I was doin' fine.

they were so inseparable and because C_{60} was always dominant (Figs. 6 and 8). As far as C_{60} was concerned, it seemed no accident that the modern soccerball with the same layout is one of the most, if not *the* most, resilient of constructs, able to survive being kicked around the world (and perhaps around the galaxy). Maybe the football held a simple clue. When I looked carefully at a football, I was struck by the fact that all the (black) pentagons are isolated, whereas all the (white) hexagons are linked. It is known that unsaturated compounds composed of abutting pentagons (the pentalene configuration, Type II, Fig. 14), without substituents which allow extended conjugation, tend to be unstable. Curiously, a compound with just such a structure appeared on the cover of *Angewandte Chemie* (July 1987) that very week.

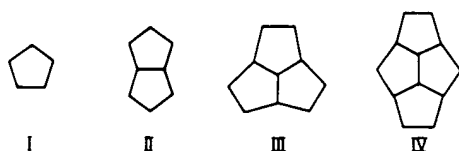


Fig. 14. Isolated and abutting pentagons: I, isolated; II, fused pair (pentalene configuration); III, symmetrically fused triplet (triquinacene configuration); IV, directly fused quartet [53].

Since Euler's law requires 12 pentagons for closure, it was also clear that C_{60} was the smallest carbon cage for which all the pentagons could be isolated. O'Brien's reactivity experiments had convinced us that closure was possible, even probable, for all the even clusters. I conjectured that a *pentagon isolation rule* could be formulated to account for the stability^[53]; then I began to wonder which was the next cage for which pentagon isolation was feasible.

By playing with the models I saw immediately that it was not C_{62} , and as I added more atoms, try as I would, I could not find cage structures for C_{64} , C_{66} , or C_{68} without abutting pentagons. We had already proposed a structure for C_{70} ,^[50] after Smalley had shown that by splitting C_{60} into two C_{30} hemispheres a ring of ten extra carbons could be neatly inserted, producing a most elegant, symmetric, egg-shaped structure (Fig. 15 right). Suddenly I realized that perhaps this C_{70} cage was the next structure after C_{60} which could close and which also had *isolated* pentagons (Fig. 15). This surprised me. Perhaps closure *necessitated* that 70 be

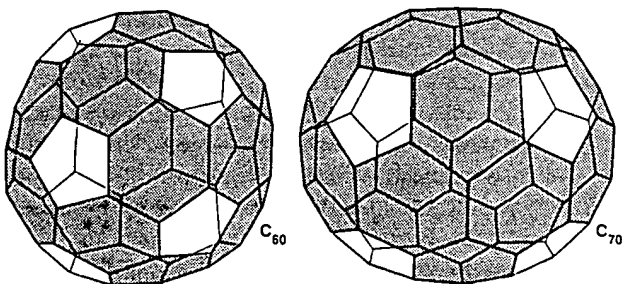


Fig. 15. For species with less than 72 atoms these two structures are the only ones which can be constructed without abutting pentagons. Thus on the basis of the *pentagon isolation principle* and geodesic considerations C_{60} and C_{70} are predicted to be the first and second magic fullerenes. This result together with Figure 8 provided the simplest and strongest circumstantial evidence supporting the closed-cage concept.

the second magic number! We had stuck our necks out with the C_{60} hypothesis on the basis of a single peak in the mass spectrum, but it now seemed that the cage concept positively insisted that C_{70} as well as C_{60} are special.^[53] That would be wonderful. A second solution which required both of these particular magic numbers was impossible to conceive, especially since 70 would be an unusual number to be deduced as magic at all, let alone the second in order. I knew that nature would not be that perverse, and thus for first time my conviction that our structure was correct became absolute, and I never again doubted that one day we would be vindicated. Indeed in my opinion this result meant that we were home and dry.

I was elated by this line of reasoning, but I really needed proof. I remembered that Tom Schmalz and his colleagues, Klein and Hite, in nearby Galveston had published some elegant graph-theoretical studies on the fullerenes. I contacted him and asked him what he thought about my idea. I was amazed and delighted when he told me that they had been looking at this same problem and had proven that cages composed of 62, 64, 66, and 68 atoms cannot be constructed without abutting pentagons.^[54] So it was true! I told him that I wondered whether the semimagic C_{50} might be the smallest cage able to avoid abutting triplets of pentagons (Type III, Fig. 14, Lit.^[53]). Schmalz et al. subsequently showed this also to be correct.^[54] One Sunday afternoon, sitting in front of the molecular models strewn all over our coffee table at home, I decided to investigate other semimagic numbers. I wondered about C_{32} which had been shown by the group at Rice University to be the first cage relatively stable towards photolysis. I toyed with the idea that it might be the smallest cage able to avoid fused quartets of pentagons (Type IV, Fig. 14). I tried to make the smallest model containing such a structure, and as I counted up the atoms I suddenly realized, that it was not C_{32} but a delightfully symmetric C_{28} cage (Fig. 16). I became excited because I

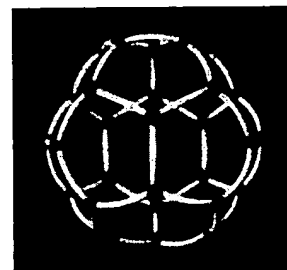


Fig. 16. Molecular model of C_{28} , one of several fullerenes (with 24, 28, 32, 50, and 70 atoms) predicted to be stable on the basis of geodesic and chemical considerations [53]. These magic-number predictions fitted almost perfectly the observations made under certain clustering conditions [51, 55] (see Fig. 17).

knew, that during the Rice/Sussex collaboration period we had occasionally obtained mass spectra in which C_{28} was almost as dominant as C_{60} . At this point it seemed that essentially all the magic numbers would fall into place if these clusters were *all* cages. In particular, I found that I could explain the fascinating spectrum (Fig. 17) published by the Exxon group.^[55] Here was all the proof I needed to convince myself that a whole family of cage molecules was sitting around waiting to be discovered. The first somewhat

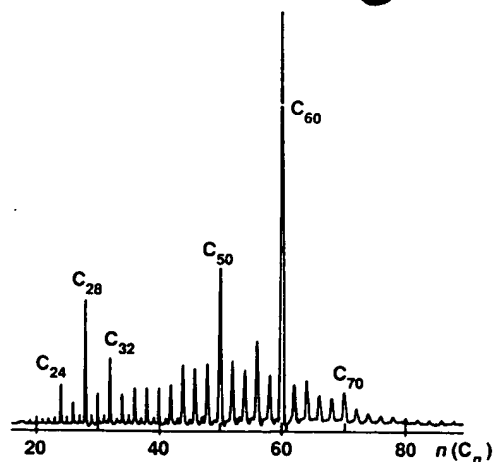


Fig. 17. The particularly interesting mass spectrum of C_n clusters obtained by Cox et al. [55]. The correspondence with the magic fullerene sequence 24, 28, 32, 50, 60, and 70 [53] was the most convincing evidence for the existence of the fullerene family prior to the extraction breakthrough. The sharp cut-off at 24 is particularly convincing, since no C_{22} fullerene can exist.

stable member of the family appeared to be C_{24} . This can be explained by the fact that C_{22} cannot exist (I am indebted to Patrick Fowler for pointing out this fact to me) and that C_{20} is the smallest cage and as it has no hexagons at all, almost certainly the least stable. To some extent C_{28} (Fig. 16) became my own personal favorite, because regardless of which of the four threefold axes one views this tetrahedral molecule along, it looks uncannily like Gomberg's famous free radical, triphenylmethyl; this also just had to be right. I knew about Moses Gomberg's discovery from my favorite organic text (Fieser and Fieser^[56] which Harry Heaney, my chemistry teacher in school, had encouraged me to buy and read so long ago). It had always amused me to think that on attempting to make the rather mundane compound hexaphenylethane, Gomberg failed (miserably), produced the triphenylmethyl radical, and had to be consoled with becoming known as the father of free radical chemistry instead. This was the sort of "failure" that really appealed to me. If C_{28} is relatively stable, then $C_{28}H_4$ should be a fairly stable hydrofullerene. This seemed not at all farfetched; after all, dodecahedrane which Paquette and co-workers first made^[57] is basically the perhydrofullerene of dodecahedrene (fullerene-20), the simplest and probably the least stable of all the fullerenes since it contains no hexagons. At this time I had a telephone conversation about nomenclature with Alex Nickon in which we came to the conclusion that the name "fullerenes" would work well for the family of carbon cages.^[40, 53] I gained much satisfaction from the refined concept which was even more appropriate, because Buckminster Fuller had patented constructs of all shapes and sizes based on the 5/6 ring principle;^[58] some were very similar to the elongated framework of C_{70} . Nickon was just finishing his entertaining book with Silversmith on the origins of the trivial names of compounds.^[40]

In Houston a particularly important series of experiments was carried out by Curl, Smalley, and their co-workers which offered further overwhelming evidence for closed cages.^[52] One of these was a photofragmentation experiment which provided even-numbered products. Curl had worked out a neat way of explaining how the cages might "spit out" even-numbered (2, 4, 6, ...) carbon chains and then reseal.

Another most convincing study showed that when the encapsulation of atoms of various sizes appeared to be successful, the smallest caged species detectable had diameters commensurate with the known sizes of the encapsulated atoms.

C_{60} and Soot

During one of my eight visits to Rice University between August 1985 and April 1987 we considered carefully the reactivity results and developed a hypothetical mechanism for the formation of C_{60} .^[45] Heath, O'Brien, and I spent hours in the library digging through an excellent selection of books and journals on carbon. The final version of the mechanism grew out of intense synergistic group discussion. It was also clear that the mechanism might explain soot formation as well. After all in a review on soot, Harris and Weiner^[59] had pointed out the complete absence of knowledge of the chemistry involved in soot formation. Thus a fresh idea probably would be welcome. Our mechanism implied C_{60} should be a by-product of soot formation. Curl was apprehensive about introducing the word soot, especially in the title. How prescient were his worries! However, Smalley and I decided to throw caution to the wind—after all, when you have gone as far as you can go (in postulating C_{60} formation in a chaotic plasma), you might as well go further. Our paper met with some criticism.^[60] To our delight, however, in 1987 we heard that Klaus Homann's group in Darmstadt discovered that C_{60} was a dominant ion in a sooting flame.^[61] (Note: Very recently, a careful study by Howard's group at the Massachusetts Institute of Technology has shown that up to 7% of the soot from a benzene flame consists of fullerenes.^[62])

The Giant Fullerenes

One day I decided to spend £300 on ten-thousand sp^2 carbon atoms (molecular models!) The odd eyebrow was raised at Sussex when I said that I was buying them just because I wanted to see what giant fullerenes such as C_{6000} (with a diameter ten times that of C_{60}) looked like. Ken McKay (a graduate student) obtained Coxeter's book^[63] and Goldberg's paper^[64] and set to work. When he came into my room with models of C_{240} and C_{540} (Fig. 18), I was delighted but perplexed—they were beautiful, but not at all what I had expected. C_{540} , in particular, was not round like Buckminster Fuller's domes, but in fact much more interesting: It was essentially a monosurface which swept between cusps in the vicinity of the pentagons; it had icosahedral symmetry, but was not an icosahedron.^[65] Then we realized that its shape might explain^[65] the polyhedral patterns in graphite microparticle electron microscope pictures published by Iijima (Fig. 19).^[66] The structure of these microparticles could be nicely explained as concentric shells of graphitic carbon in which the shells had giant fullerene shapes. Few of our discoveries have delighted me more than these objects, partly because they are so elegant, but also because the exercise, which was started *purely* for fun and with no serious aim, had yielded such an apparently important result. It was also an object lesson, since I had assumed



Fig. 18. Molecular models of the giant fullerenes C_{240} (left) and C_{360} (right). The models possess icosahedral shapes rather than perfectly spheroidal ones similar to the geodesic domes. Each of these structures can be considered as an initially flat hexagonal network which has warped into a closed monosurface (of icosahedral symmetry) by 12 pentagonal disclinations giving rise to the cusps.

that the giant fullerenes would be spherical like Buckminster Fuller's domes and had not looked carefully at Iijima's images. Even the most spheroidal giant fullerene (Fig. 19a) was clearly polyhedral (Fig. 19b). To see what one wants to see

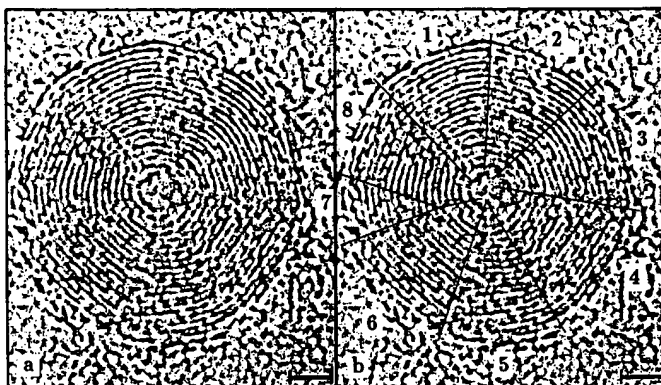


Fig. 19. The image obtained by electron microscopy of an onionlike graphite microparticle observed by Iijima [66] which appears superficially to be spheroidal (a). Careful scrutiny of this image, however, indicates that the object has a polygonal outline consistent with a set of concentric quasi-icosahedral fullerene-like shells (b) [65]. The marker indicates a scale of 20 Å.

rather than what is, is a cardinal sin for a scientist and the temptation is to be resisted at all costs.

The Quest for C_{60}

Until late 1989 the evidence in support of our structure proposal was, to my mind, very convincing, but it could not be deemed anything other than circumstantial. Clearly a macroscopic sample of C_{60} was needed—not just a whisper in a supersonic helium wind, detectable only by that ultra-sensitive sensor, the mass spectrometer. At Sussex we sought more tangible evidence. The Science and Engineering Research Council (SERC) funded the construction of a cluster-beam apparatus, which was assembled with Tony Stace; Steve Wood helped us to obtain financial support from

British Gas in the form of Collaborative Award in Science and Engineering (CASE) studentship for combustion-related studies. It was this assistance which was ultimately our salvation (*vide infra*). In a third project conducted with Ken McKay, we probed (by electron microscopy) the films produced by a carbon arc under helium in an old bell jar evaporator. We found that the film microstructure changed as the helium pressure was increased (to ca. 50 mmHg). The quadrupole mass spectrometer, with which I sought to monitor whether C_{60} was produced in this experiment, was the integral part of a modest carbon materials research project which failed to attract support from any funding source (including chemical companies). Because Stace and I had been quite generously funded by the SERC solely for the cluster-beam studies, another application (and indeed a rather applied one) to that source was difficult. Time slipped by and this program faltered even though I had put a great deal of effort into trying to obtain financial support.

The First Paper by Krätschmer, Fostiropoulos, and Huffman

In September 1989 Michael Jura (UCLA Astronomy Department) sent me a copy of a thought-provoking paper^[67] (Fig. 20) presented by Krätschmer, Fostiropoulos, and Huffman at a symposium on interstellar dust. This research group from Heidelberg and Tucson had observed four weak but distinct infrared absorptions in a film of arc-processed graphite, which were tantalizingly consistent with the expected spectrum of buckminsterfullerene. From theoretical studies^[68] it was known that C_{60} should exhibit only four lines. What was more, the observed frequencies agreed quite well with those predicted. I had long followed the work of this group and knew that they had developed great expertise in studying carbon by spectroscopy. We had occasionally tried related studies, and I was only too aware of how tricky they were. I was sceptical about their result and also rather cha-

Harry - Presented at Capri -
do you believe this? -m.

SEARCH FOR THE UV AND IR SPECTRA OF C_{60} IN LABORATORY-PRODUCED CARBON DUST

W. Krätschmer, K. Fostiropoulos, Max-Planck-Institut für Kernphysik, Heidelberg, W.-Germ. and

D.R. Huffman University of Arizona, Tucson, Arizona, USA

Carbon dust samples were prepared by evaporating graphite in an atmosphere of an inert quenching gas (Ar or He). Changes of the spectral features of the carbon dust were observed when the pressure of the quenching gas was increased. At low pressures (order 10 torr), the spectra show the familiar broad continua. At high pressures (order 100 torr), narrow lines in the IR and two broad features in the UV emerge. The four strongest IR features are located in the vicinity of the lines predicted for the C_{60} molecule. One of the observed UV features may be related to the known 368 nm transition of C_{60} . It thus appears that at high quenching gas pressures C_{60} is produced along with the carbon dust.

Fig. 20. Annotated copy of the key paper presented by Krätschmer, Fostiropoulos, and Huffman at the conference *Dusty Objects in the Universe* in Capri (1989) [67]. This paper with the appended query was sent to me by Michael Jura (UCLA) who attended this conference.

grined, for had not Ken McKay made soot in a bell jar in exactly the same way three years before during the project, which we were forced to abandon through lack of funds?

I decided to resurrect the old and decrepit bell jar and with Jonathan Hare (holder of the British Gas CASE graduate studentship) tried to reproduce the infrared features obtained by Krätschmer et al. Michael Jura's missive arrived around September 1989, just before the start of the Sussex academic year, a time when third year undergraduate projects are needed. It does not matter whether these projects yield results; they should imbue the student with the flavor and excitement of genuine research, that is, the experience of working in the dark, not—as all too often happens—the frantic scramble for results at all costs! I had often initiated the most speculative of projects in this way, and my experience had shown time and time again that important and exciting studies could often start from such inauspicious beginnings. It seemed perfect for Amit Sarkar's third-year project, and he joined Hare on this wildly speculative project. Fairly soon these students succeeded in obtaining the IR bands (Fig. 21), which, although always very weak and highly irreproducible, confirmed the observations of the group from Heidelberg and Tucson. The obsolete apparatus then

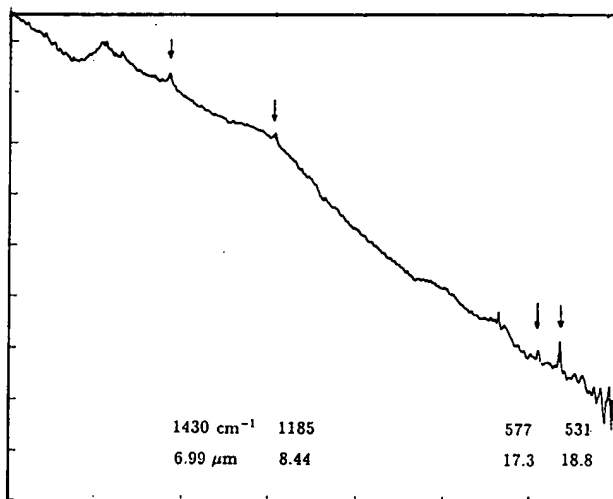


Fig. 21. Infrared spectrum of a film of arc-processed carbon obtained by Hare and Sarkar at Sussex which shows weak but clear (and confirmatory) evidence that the features first observed by Krätschmer et al. [67] (see Fig. 20) and tentatively assigned to C_{60} were real and repeatable.

promptly fell to pieces! After rebuilding it almost completely from scratch, Hare tried to repeat the earlier observations, but consistent results eluded him. Sometimes he obtained the characteristic spectral features, sometimes they disappeared for days or weeks at a time. In retrospect, I suspect that the original discovery of the IR features by Krätschmer et al. could have been made by few other groups. Hare carefully varied every experimental parameter he could think of and finally developed the expertise to produce films which exhibited the telltale infrared features consistently. He wrote to Krätschmer about his efforts and received an encouraging reply containing useful advice. This certainly helped, because it was quite difficult to make films amenable to analysis.

The Dimerization of C_{30}

I spent about one month in the UCLA Astronomy Department around Easter 1990. One day, Mark Morris brought François Diederich from the Chemistry Department to see me. Diederich appeared excited and exhorted me to come to his office because he had something to show me. In response to his manner I somewhat disdainfully quipped, "You've not made C_{60} ?" When he replied, "How do you know?" I was startled and suddenly became apprehensive since there was genuine surprise in his voice. When we arrived at his office he showed me an astonishing mass spectrum. In their attempts to make a pure carbon ring of 30 atoms Diederich, Rubin, Whetton, and their co-workers, had found that the molecule spontaneously dimerized to form C_{60} with almost unbelievable efficiency.^[69] This staggering result seemed to answer, almost at a stroke, many puzzling questions that had been on my mind for years about carbon chains, their relationship with C_{60} , and soot. But I became even more apprehensive when I comprehended that the UCLA group might be on the verge of obtaining the coveted C_{60} NMR line. Subsequent discussions with David Walton, with whom I had probed aspects of the C_{60} formation mechanism,^[70] alleviated my worries; he convinced me that scaling up the UCLA experiment so as to produce sufficient C_{60} for the key NMR measurement presented an enormous challenge.

Mass Spectrometry

I returned to Sussex and by early summer 1990 started to believe for the first time that C_{60} really might be in our sooty deposit. We therefore decided to probe the material by solid-state magic-angle-spinning (MAS) NMR. Indeed Ken Seddon (a Sussex colleague) had encouraged me to do this some years before. Perhaps the single ^{13}C NMR line was close at hand in the black soot, which at least we could now touch. I considered buying the most isotopically pure ^{13}C graphite, but that would have been very expensive, and we had no

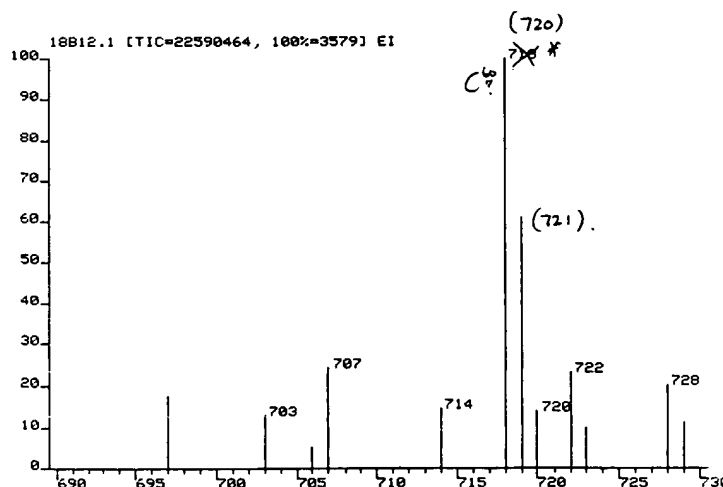


Fig. 22. Part of the FAB mass spectrum of a deposit of arc-processed soot obtained by Abdul-Sada on July 23rd, 1990 at Sussex. The calibration was off by 2 amu; however, the isotope pattern was convincing since the peaks are close to the intensity ratio 1.0/0.66/0.44 expected for $^{12}C_{60}/^{12}C_{59}/^{13}C_{58}$.

money anyway. The problem of generating enough material for solid-state NMR from the scrapings of thin sooty films, seemed insurmountable, especially since it was so difficult to produce the films in the first place, let alone analyze them. We really needed another way to monitor the samples, so we tried Fast Atom Bombardment (FAB) mass spectrometry. Ala'a Abdul-Sada helped us, and finally we obtained the mass spectrum shown in Figure 22. The signal containing the ^{13}C satellites was really quite convincing, but I wanted the result confirmed. The entry in Jonathan Hare's laboratory notebook on July 26th, 1990 (Fig. 23 top, second sentence) epitomizes many of our problems and requires little further comment.

The Red Solution

During this period we had considered the properties of C_{60} . What form would the compound take? Would it be a high-melting solid or a liquid? Would it be soluble? Benzene was an obvious solvent, since C_{60} should look like benzene from every side (or at least from 20 sides). I remembered the little pink (or yellow) vial of liquid we used to talk about and wondered if the compound might even be volatile. In addition I had often discussed (with Smalley, Rohlfing, and oth-

ers) how much C_{60} was being made in our experiments. The rough proportion which always seemed to arise was $< 1/10000$ of the total amount of carbon. At this level, given the amount of soot available, only a supreme optimist would attempt solvent extraction. Fortunately Hare is one—perhaps partly because he is a physicist working among chemists. On Friday, August 3rd Hare made up a mixture of the soot and benzene in a small vial, which he set aside over the weekend (Fig. 23, second entry). When he came in on Monday morning (August 6th) he noted (Fig. 23, third entry) that the solution looked "slightly red(d)ish" (Fig. 24). The generation of a red solution from pure carbon was scarcely believable. Hare made more material during the next few days and attempted mass spectrometric measurements on extracted material for the first time on Thursday, August 9th (Fig. 23, fourth entry).

possible use of FAB Mass Spect 26/7/90.
Came back from Scotland Walk to find fab Mass spec had been done with exciting results. Unfortunately the machine has broken down so we can't repeat.
Results so far.
Seen decent signal @ $(12 \times 60) = 720 \text{amu}$!
also ^{13}C is ~1% of natural carbon so calculations show that for C_{60} we 60% could have Dne

3/8/90
1) Made approx $\frac{1}{2}$ a (30ml) tube of C_{60} + Carbon powder, Actual Volume would be much smaller than this because powder is so uncompact.
2) added about 25ml of Benzene and shook mixture.
3) allowed to stand for Weekend.

6/8/90

Solution looks slightly reddish, tried to pipet liquid out from top but mixed up.

9/8/90

Vacuum lined sample to about 5th of Volume could go lower (ie more concentrated) but we used about this Volume if we want to use the liquid cell, so will keep to this.

Continued evaporation down to about 4-5 drops (unk?). FAB showed $\text{No } \text{C}_{60}$ (720).

Fig. 23. Entries by Hare in his laboratory notebook: July 26th, 1990; August 3rd, 1990; August 6th, 1990; August 9th, 1990.

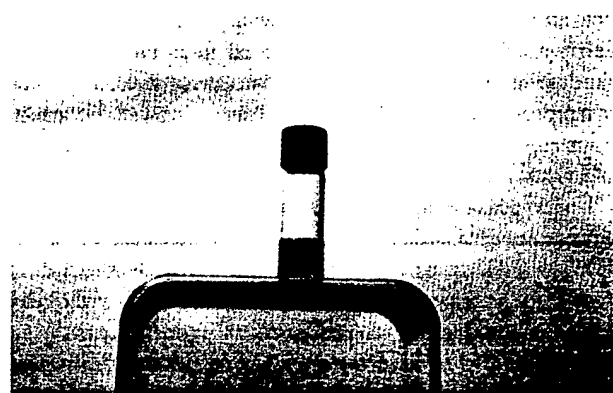


Fig. 24. Original reddish extract obtained on Monday, September 6th, 1990 (see Fig. 23).

About 10 o'clock the next morning (Friday, August 10th) I received a telephone request from the journal *Nature* to referee a paper by the Heidelberg/Tucson group which I accepted. I was totally unprepared for the bombshell which arrived minutes later by telefax. Following up their own earlier work, Krätschmer, Lamb, Fostiropoulos, and Huffman had successfully sublimed from their carbon deposit a volatile brown material, which dissolved in benzene to give a RED SOLUTION (!!!!!).^[71] Crystals obtained from this solution yielded X-ray and electron-diffraction data commensurate with material composed of arrays of spheroidal molecules 7 Å in diameter separated by 3 Å, just as expected for buckminsterfullerene. This beautiful paper even contained photographs of crystals. I was convinced that they had isolated C_{60} , and we had been pipped at the post. Somewhat stunned, I pondered our demise and faxed my report back to *Nature* after lunch. I recommended that the paper be published without delay and requested the editor to convey my sincere congratulations to Krätschmer and his associates.

This was what the British call a difficult moment, but as I slowly surveyed the damage I realized that all was not quite lost. It gradually dawned on me that there was not a single(!) NMR line to be seen in the manuscript (nor was there a mass spectrum. We later learned that they had the mass spectrum, but certain problems had arisen which precluded its inclu-

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sion in the manuscript.) At this point we had spent nearly a year struggling independently learning how to make the arc-processed material; we had made our own soot, we had confirmed the presence of C_{60} mass spectrometrically, and we had solvent-extracted the red material—and all this *before* the manuscript arrived. I decided that we were not going to abandon our efforts now after we had achieved all this. We still had a lot going for us, and I thought we might be able to obtain the desired NMR result. However, now that the Heidelberg/Tucson study was essentially in the public domain it would be transmitted around the world by telefax within hours. I had studiously tried to avoid such situations in science—competition—all my life; my philosophy is to probe areas in which few others, preferably no one, work. That is where, it seems to me, the most unexpected discoveries are likely to be made.

We had to act very quickly if five years of effort were not to be completely in vain. A race must be on because the material was now so easy to make, and it could not be long before other groups, far better equipped than we, recognized that there was one last exquisite prize remaining in the story of the discovery of C_{60} —the NMR line. Our one priceless advantage was that Hare had already made a reasonable quantity of material, and that, at that moment, only the Heidelberg/Tucson group had any at all. We needed help and fast. Roger Taylor, an organic chemist, provided the desperately needed expertise; he separated the material quickly and efficiently. Since our mass spectrometer had broken down again, Hare rushed by train to Manchester with a sample of the precious extract. Numerous frantic telephone calls passed between Sussex and Manchester, because the sample refused to respond to analysis. Then with a key piece of

fullerenes with 56 to 72 atoms were detected: in particular, C_{70} was abundant. The whole family of fullerenes appeared to be present in the soot, not just C_{60} !

C_{60} is Magenta (Pink?) in Solution

Taylor noted that the extract was soluble in hexane and recognized that he might be able to separate the fullerenes chromatographically. To his delight he found that on an alumina column resolution into two bands, one red, the other magenta, could be achieved. The magenta fraction, (Fig. 26) was a delight to the eye in the delicacy of its color.

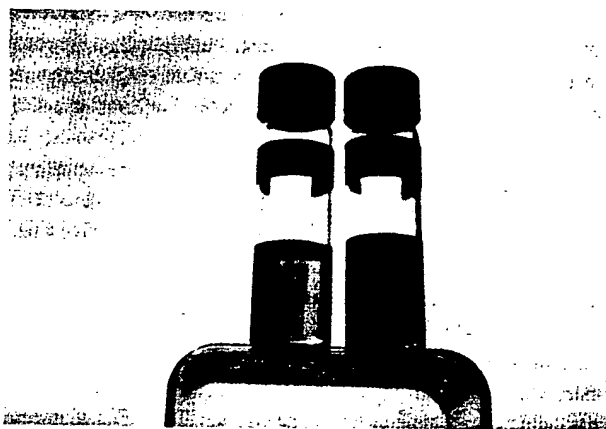


Fig. 26. Chromatographic separation of the red extract by Taylor resulted in a magenta C_{60} fraction (left) and a red C_{70} fraction (right).

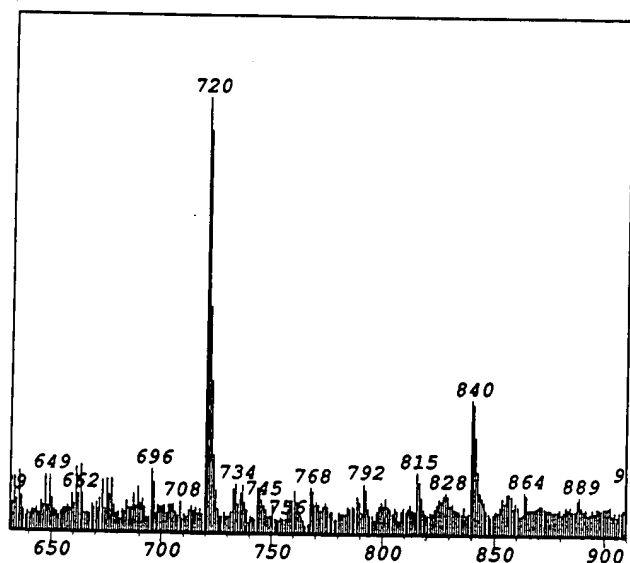


Fig. 25. Part of the FAB mass spectrum of the red extract which confirmed that it consisted mainly of C_{60} and C_{70} . The spectrum also indicates the presence of other fullerenes [72].

advice from Taylor about solubility, the Manchester operators (at Kratos) managed to dissolve the material in the FAB matrix and obtained the FABulous mass spectrum shown in Figure 25. It was hard to believe, but besides C_{60} other

Its mass spectrum showed a peak at 720 amu, and we sent the sample to Tony Avent for NMR analysis. We were summoned to see our single line (Fig. 27), which Avent assured

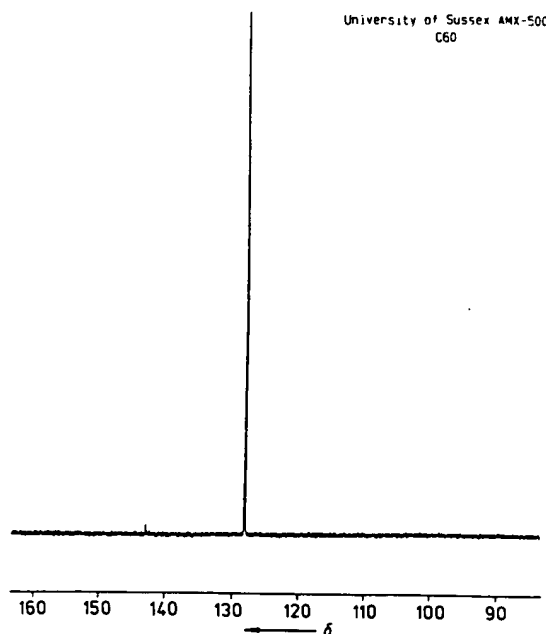


Fig. 27. The first NMR spectrum in which the C_{60} resonance (at $\delta = 143$ ppm) was first identified (barely). The strong line at $\delta = 128$ ppm is (rather appropriately) the resonance of benzene.

us was present. So this was it: a line so small I needed a microscope to see it! Could this insignificant little blip really be the line I had dreamed about for five years? Further work confirmed beautifully that this was the result which we had sought for so long.^[72] The joy alleviated almost all the despair I had first felt on reading the paper by Krätschmer et al. One might have thought, as some said, that I should have been pleased to have been proven right when so many had been sceptical. That was not my feeling, probably because I had known ever since the recognition of C_{70} as the second magic fullerene^[51] that our structure could not possibly be wrong. I know that my colleagues at Rice University also had no doubts.

What about C_{70} ? It turned out to be the icing on the cake, although not without attendant trauma. The wine-red fraction which had masked the pale magenta of C_{60} yielded a mass spectral peak at 840 amu and was clearly C_{70} . According to the expected structure (Fig. 15 right) this compound should exhibit a ^{13}C NMR spectrum with five lines. On Sunday, September 2nd, 1990 I entered the laboratory at the same time as Avent who told me the C_{70} measurement should have just been completed. The spectrum we plotted was sensational—or almost so. There were indeed five lines, but one was in the same position as the C_{60} peak. Could it be that one line was underneath the C_{60} signal? After repeat-

ed chromatography to remove the last vestiges of C_{60} , further NMR studies showed the fifth line to be rather different from the others. The resonance of the ten atoms in the waist (Fig. 28c) is more "benzenoid" than the other four resonances.^[72] Indeed this line lies dangerously close to the benzene solvent line; had it been a little closer to the benzene signal it would have been swamped and missed altogether. In many ways the five lines of C_{70} are (arguably) more important and significant than the C_{60} singlet. For one thing, they confirm that fullerene carbon atoms are not fluxional; for another, they show that the atoms are not on the perimeter of a monocyclic ring. Both of these cases would lead to a spectrum with a single resonance. Even more important was the fact that the NMR results confirmed the family concept for fullerene cages. It was now clear that a host of stable fullerenes were just waiting to be discovered, as we had long suspected.^[53]

"The Third Man" is as Elusive as Ever in Space

The elusiveness of C_{60} and my belief that it has been lurking in that blackest of black materials, soot, since time immemorial often reminded me of the role played by Orson Welles in the film "The Third Man". The spirit of this anti-hero pervades the whole movie although he is seldom seen. Indeed he makes his first appearance late on in the movie in the black shadows of a dark street in Vienna when his face is suddenly illuminated by a light being switched on. For five years C_{60} played a very similar shadowy role—at least as far as I was concerned. My part in the buckminsterfullerene story really started out in space, and this celestial sphere has come down to earth with more of a bounce than a bump; but will it bound back up into space? Is this third form of carbon distributed ubiquitously in space as we surmised the day we found it in the laboratory?^[41] Now that we know something about fullerene-60, we should be able to study all its optical properties. It is clear that the UV radiation density in the optically observable interstellar medium is such that the species will be ionized.^[73] The possible existence of encapsulated complex ions^[73, 74] is quite interesting. However, even with buckminsterfullerene in our hands, we find that this "third man" is as elusive as he ever was in the space between the stars. Perhaps the interstellar form is related to protonated carbon monoxide (HCO^+), which Bill Klemperer identified about 20 years ago.^[71] If there are any C_{60} molecules in space there can be little doubt that most will have a proton or some other atom adhering to their surface.^[74] $C_{60}\text{H}^+$ could probably survive for eons. Other abundant elements, particularly alkali and alkaline-earth metals, must also stick to the surface. Such species will have fascinating optical spectra. For instance, the energy and wavelength of the charge-transfer transition $(C_{60}^+)X \rightarrow (C_{60})X^+$ can be estimated to a first approximation as simply the difference between the ionization potentials of the separated species. For $(C_{60}\text{H})^+$ this transition lies at about 2200 Å. For $(C_{60}\text{Na})^+$ and $(C_{60}\text{K})^+$ the transitions lie in the region of the Diffuse Interstellar Bands^[33] and for $(C_{60}\text{Mg})^+$ near zero frequency(!) These observations imply that this and related species will have unusual electrical properties. These processes are probably related to the recently observed superconductivity

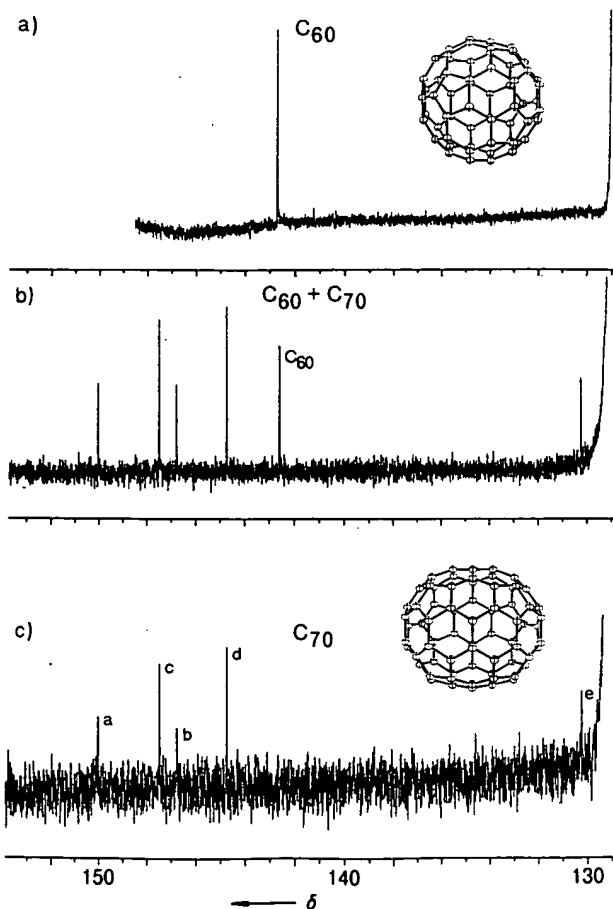


Fig. 28. ^{13}C NMR spectra obtained from chromatographed samples of soluble material extracted from arc-processed graphite: a) spectrum of purified C_{60} (magenta fraction); b) mixed C_{60}/C_{70} sample; c) spectrum of purified C_{70} (red fraction) showing five lines as expected for the symmetric egg-shaped molecule (see Fig. 15).

of metal-doped fullerene-60 materials.^[75] This conjecture is supported by an important new result which comes not from work with bulk material but from cluster-beam studies by McElvaney and Callahan.^[76] They found that the gas-phase proton affinity of C_{60} is similar to that of ammonia—a remarkable result! I like to put my trust in intuition: when all else fails it is, after all, our only guide. It is curious to note that some important spectral features of space (the Diffuse Bands) have been visible for decades, yet we do not know what causes them. Now we have discovered that an unexpected molecule, C_{60} , has been under our noses on earth since time immemorial and was invisible until now. It seems to me highly likely that these two observations will turn out to be connected.

Epilogue

Since the time that graphite balloons and C_{60} were twinkles in the eyes of David Jones, Eiji Osawa, and a few other imaginative scientists,^[42, 43, 46–48] there have been many significant contributions, both experimental and theoretical, to the first chapter of the buckminsterfullerene story which has just been completed. These have recently been comprehensively reviewed.^[77] Figure 12 shows the Rice/Sussex team and Figure 29, the Sussex Buckaneers. These two teams together with the Heidelberg/Tucson team scored many of the goals in the football match which has just ended. Many new teams have now started to play an exciting, but different, ball game. The important difference is that the players can now see what they are kicking.



Fig. 29. The Sussex Buckaneers football team. From left: Kroto, Abdul-Sada, Taylor, Hare, and Walton.

Apart from the successful observation of the "lone" NMR line, two other matters give me a sense of deep pleasure: one was the beautiful color of C_{60} and, furthermore, that it was seen first at Sussex. The second was that apparently no one else appeared to have followed up the early IR results obtained by the group from Heidelberg and Tucson (September 1989). In retrospect I find this astounding; perhaps it was because the work appeared in the astronomy literature, but more likely it was because research today is carried out under

such pressure, and our fear of failure is so great (and exacerbated by funding procedures). Few groups enjoy the luxury of working in the dark—a condition which I feel lies at the heart of true scientific endeavor. I have a videotape of a marvellous BBC documentary on Richard Feynman (the greatest lecturer I had ever heard) from the series "Horizon". In one part he talks on essentially this topic. This 50 minute program had the most profound effect on me. At one point Feynmann described how, when he was hired at Cornell, Bob Wilson had told him that it was the university's responsibility whether he accomplished anything—it was their risk(!) It was not for Feynman to worry about, he should amuse himself. In this way he was freed from the psychological burden of doing anything "important", and he was able to relax and do what he most enjoyed—physics and mathematics—just for the fun of it. How lucky he was. I know of few professional scientists today, certainly no young ones, who are in such a utopian scientific environment. What a sad reflection on today's research, especially since we know in our hearts that human beings achieve most when they are free of pressure. We know that small children learn and discover the joys of nature most efficiently during their play.

News of the breakthroughs spread like wildfire during September 1990, and the method of production developed by the Heidelberg/Tucson group was immediately improved upon^[78] at Rice University. As soon as it was known that fullerenes are chromatographically separable and that solution NMR is feasible, other groups confirmed these measurements.^[79, 80] Don Huffman remarked laconically at a recent symposium, "Everyone is able to repeat these experiments".

A new postbuckminsterfullerene world of round organic chemistry and materials science has been discovered overnight. Almost every day a new paper appears on some novel aspect of fullerene behavior. The group from Rice University has shown that C_{60} forms species such as $C_{60}H_{36}$.^[78] Hawkins et al. have made an osmium complex in which the spinning of the fullerene ball is stopped and has enabled accurate bond lengths to be determined.^[81] NMR studies by Yannoni et al. have also yielded accurate bond lengths.^[82] The radical anion has been polymethylated by Olah's group;^[83] platinum complexes have been prepared at DuPont.^[84] At AT&T it has been found that the metal-doped material now holds the temperature record for molecular superconductivity.^[75] Fascinating differences in the crystal structure of C_{60} have been found which depend upon how the crystals are produced.^[77] Foote and co-workers at UCLA have shown that C_{60} transfers light energy efficiently to generate singlet oxygen.^[85] Diederich, Whetten, and co-workers have evidence for oxides such as $C_{70}O$.^[86] C_{60} is decomposed by light under circumstances which still need to be fully identified.^[87] Also interesting is the fact that more fullerenes, such as C_{76} and C_{84} , are being extracted and characterized.^[86] The fullerene family has arrived in force, and there are balls of all shapes and sizes for everyone to play with.

This advance is an achievement of fundamental science, not applied science, and serves as a timely reminder that fundamental science can achieve results of importance for strategic and applied areas. The origin of the whole program lay in an interest in aspects of molecular dynamics, allied

with the quest for an understanding of the origin of the carbon chains in space and their possible relationship to circumstellar and interstellar grains as well as soot.^[1] These ideas welded together beautifully with the major advance in cluster science brought about by the experimental techniques developed by Smalley and co-workers at Rice University. Krätschmer and Huffman and co-workers were originally motivated by an interest in space dust and, in their recent breakthrough, by astrophysical implications of C₆₀. The C₆₀ story has many facets, but more than anything else it is yet another archetypal lesson on the benefits to be gained by supporting pure fundamental science. The field has exploded, and its applications in chemistry and the science of materials are only just starting to be explored. Finally it is worth noting that C₆₀ might have been detected 20–40 years ago, perhaps in a sooting flame; one wonders why it took so long.

Another lesson may be learned from these acknowledgements. Important contributions were made in research programs at the University of Sussex (Brighton, UK), the National Research Council (Ottawa, Canada), Rice University (Houston, Texas, USA), the Max-Planck-Institut für Kernphysik (Heidelberg, Germany) and the University of Arizona (Tucson, USA). The discovery of C₆₀ is a tribute to not only the international nature of science but also the necessity of interdisciplinary cooperation. The contribution from the University of Sussex to the story started as a consequence of the "Chemistry by Thesis" degree course initiated by Colin Eaborn, which enabled undergraduates (such as Anthony Alexander) to carry out research with supervisors from more than one field. It could only have been successful in the interdisciplinary scientific research and teaching environment which the university pioneered when Sussex was founded in the "optimistic 60s". Sadly this and other courses have been "regulated" out of existence by bureaucrats who have little understanding of how student research expertise is brought to maturity and no awareness of the dire consequences for our future scientific capability. The first part the story could also not have been achieved had chemistry at Sussex been divided into those traditional subsections of organic, inorganic, and physical chemistry. I also had close contacts with astronomers at Sussex, particularly Bill McCrea and Robert Smith. The carbon discoveries resulted from a free-wheeling research program which started with synthetic chemistry (with David Walton, Anthony Alexander, and Colin Kirby) and moved via spectroscopy and quantum mechanics to radioastronomy (with Takeshi Oka, Lorne Avery, Norm Broten, and John MacLeod at the NRC). It moved back to the laboratory and chemical physics (with Jim Heath, Sean O'Brien, Bob Curl, and Rick Smalley at Rice University). In the last phase, key advice came from Michael Jura (an astronomer) which initiated some basic chemistry (with Jonathan Hare, Amit Sarkar, Ala'a Abdul Sada, Roger Taylor, and David Walton). Apart from those mentioned in the text who played direct (and sometimes crucial parts) such as Steve Wood of British Gas, I also acknowledge greatly the help of many others who played indirect parts, particularly graduate students and post-doctoral fellows as well as colleagues such as Tony Stace, Roger Suffolk, and Mike Lappert. Finally I wish to thank Ed Wasserman for some invaluable advice and David Walton in particular for his unfailing help throughout the period of this story and his painstaking assistance in preparing this account.

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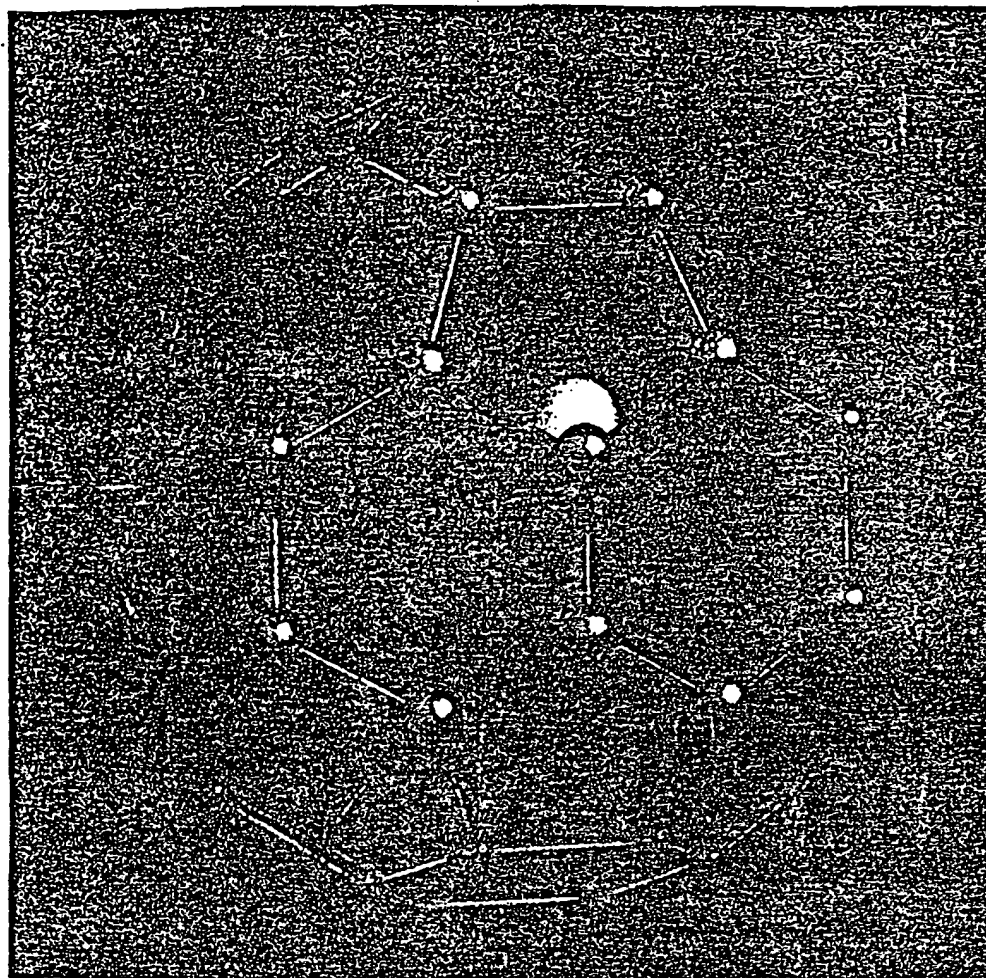
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SCIENTIFIC AMERICAN

Remnants of a planet that failed to form.

Still no technological fix for oil spills.

What made higher life-forms possible?



Buckyball, the third form of pure carbon, cages an atom in its lattice.

Fullerenes

These cage-like molecules constitute the third form of pure carbon (the other two are diamond and graphite). C_{60} , the archetype, is the roundest molecule that can possibly exist

by Robert F. Curl and Richard E. Smalley

In May of 1990 Wolfgang Krätschmer and his student Konstantinos Fostiropoulos carefully mixed a few drops of benzene with a specially prepared carbon soot. The clear solvent turned red.

Excitedly, the two workers for the Max Planck Institute for Nuclear Physics in Heidelberg telephoned their collaborators, Donald Huffman and Lowell Lamb of the University of Arizona in Tucson, who quickly repeated the experiment. The excitement continued as the two groups communicated daily by telephone and fax, exchanging measurements of the material—its infrared and ultraviolet spectra, its X-ray diffraction pattern and its mass spectrograph. Yes, the values all matched those predicted for the 60-atom carbon cluster buckminsterfullerene.

Even though some theorists had argued that this hollow, soccerball-shaped molecule should be detectable in abundance in such everyday circumstances as a candle flame, the German-American team had actually found it, succeeding where all others had failed. They were the first to observe this roundest of all round molecules, and they knew that chemistry books and encyclopedias would never be quite the same. Now there were three known forms of pure carbon: the network solids, diamond and graphite, and a new class of discrete molecules—the fullerenes.

When we heard of this breakthrough a few months later in Texas, we cele-

brated, with champagne all around. For although we had to some extent been scooped, we had been vindicated as well. Five years earlier we had had our own Eureka! experience. Together with our colleague Harold W. Kroto of the University of Sussex and our students James R. Heath and Sean C. O'Brien, we had found that C_{60} could be made in a uniquely stable form simply by laser-vaporizing graphite in a pulsed jet of helium. We had gone on to propose that this extraordinary stability could be explained by a molecular structure having the perfect symmetry of a soccerball. Because the architectural principle also underlies the geodesic dome invented by the American engineer and philosopher R. Buckminster Fuller, we named it buckminsterfullerene, or buckyball for short.

In addition to C_{60} , another molecule, C_{70} , appeared to be quite special in these early experiments. We soon found that the stability of C_{70} could be understood if the molecule had also taken the form of a geodesic dome. As Fuller had pointed out, all such domes can be considered networks of pentagons and hexagons. The 18th-century Swiss mathematician Leonhard Euler calculated that any such object must have precisely 12 pentagons in order to close into a spheroid, although the number of hexagons can vary widely. The soccerball structure of C_{60} has 20 hexagons, whereas the structure we proposed for C_{70} has 25, producing a shape reminiscent of a rugby ball.

In fact, we had found that all the even-numbered carbon clusters greater than about 32 atoms in size were remarkably stable (although less so than 60 or 70), and the evidence soon led us to postulate that all these molecules had taken the structure of geodesic domes. Again, in honor of Fuller, it seemed fitting to term this entirely new class of molecules the "fullerenes."

We later learned that such molecules had already been imagined. David E. H. Jones, writing under the pseudonym

"Daedalus" in the *New Scientist* in 1966, had conceived of a "hollow molecule" made of curled-up graphitic sheets. Others had predicted the stability of C_{60} from calculations and tried—unsuccessfully—to synthesize it. We, however, were apparently the first to discover that the material could form spontaneously in a condensing carbon vapor.

Although our evidence was sound and our conclusions were supported by extensive further experiments and theoretical calculations, we could not collect more than a few tens of thousands of these special new molecules. This amount was plenty to detect and probe with the sophisticated techniques available in our laboratory, but there was not enough to see, touch or smell. Our evidence was indirect, much as it is for physicists who study antimatter. For now, the fullerenes existed only as fleeting signals detected in our exotic machines. But as chemists, we knew that the new material ought to be perfectly stable. Unlike antimatter, the geodesic forms of carbon should be quite safe to hold in one's bare hand. All we had to do was make more of them—billions and billions more.

Thus, for five years, we had been searching for a method of producing visible amounts of the stuff. We called our efforts "the search for the yellow vial" because quantum calculations for such a soccerball-shaped carbon molecule suggested it would absorb light strongly only in the far violet part of the spectrum. We were not alone. Our initial "soccerball"

HYPERFULLERENE STRUCTURE called a Russian egg is expected to form along with ordinary fullerenes in a laser-vaporized carbon plume. Shown here is the most symmetric form: a C_{80} at the core is encapsulated by fullerenes having 240, 540 and 960 atoms. This process could continue indefinitely to produce a macroscopic particle whose pentagons are in icosahedral alignment.

ROBERT F. CURL and RICHARD E. SMALLEY of Rice University have collaborated for the past seven years in research on carbon and semiconductor clusters in supersonic beams. Curl is a professor in, and chairman of, the department of chemistry. Smalley is the Gene and Norman Hackerman Professor of Chemistry and a professor of physics. For the past five years, he has also served as the chairman of the Rice Quantum Institute.

proposal, published in *Nature* in 1985, had made the quest one of the hottest in chemistry.

In our laboratory we collected the sooty carbon produced by the vaporization laser while using various chemical techniques to detect the presence of C_{60} . We shurried the soot in benzene, for example, and looked for a yellow color. But the solution in our test tubes stayed clear, with boring black soot sitting on the bottom. The community of cluster chemists ran many more sophisticated experiments but achieved no better result.

Many gave up hope of ever seeing the yellow vial. They reasoned that although the fullerenes may be stable, it was too hard to separate them from the other sooty material being produced in the vaporization experiments. Per-

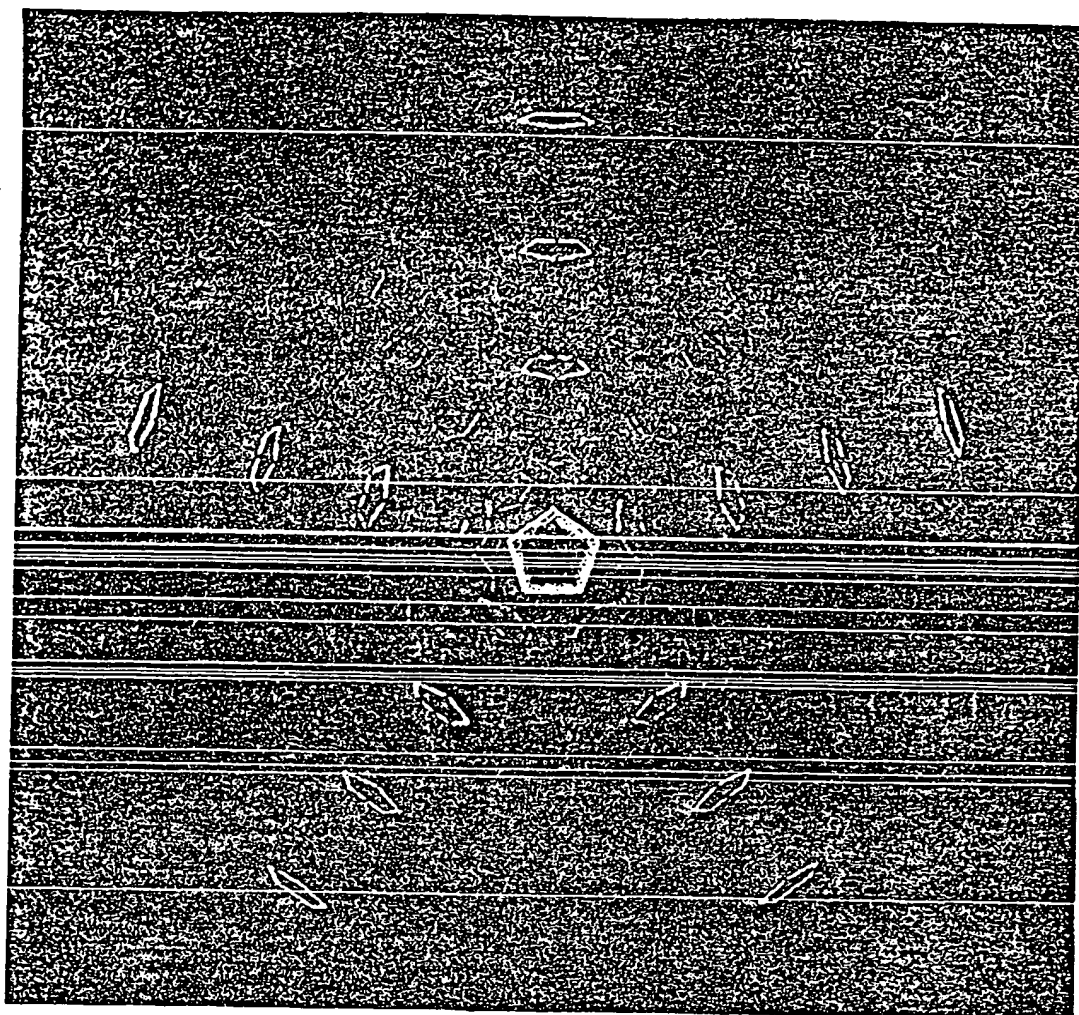
haps, the workers said, some dedicated chemist might one day extract a few micrograms with some special solvent, but no one seriously expected C_{60} to be available in bulk anytime soon.

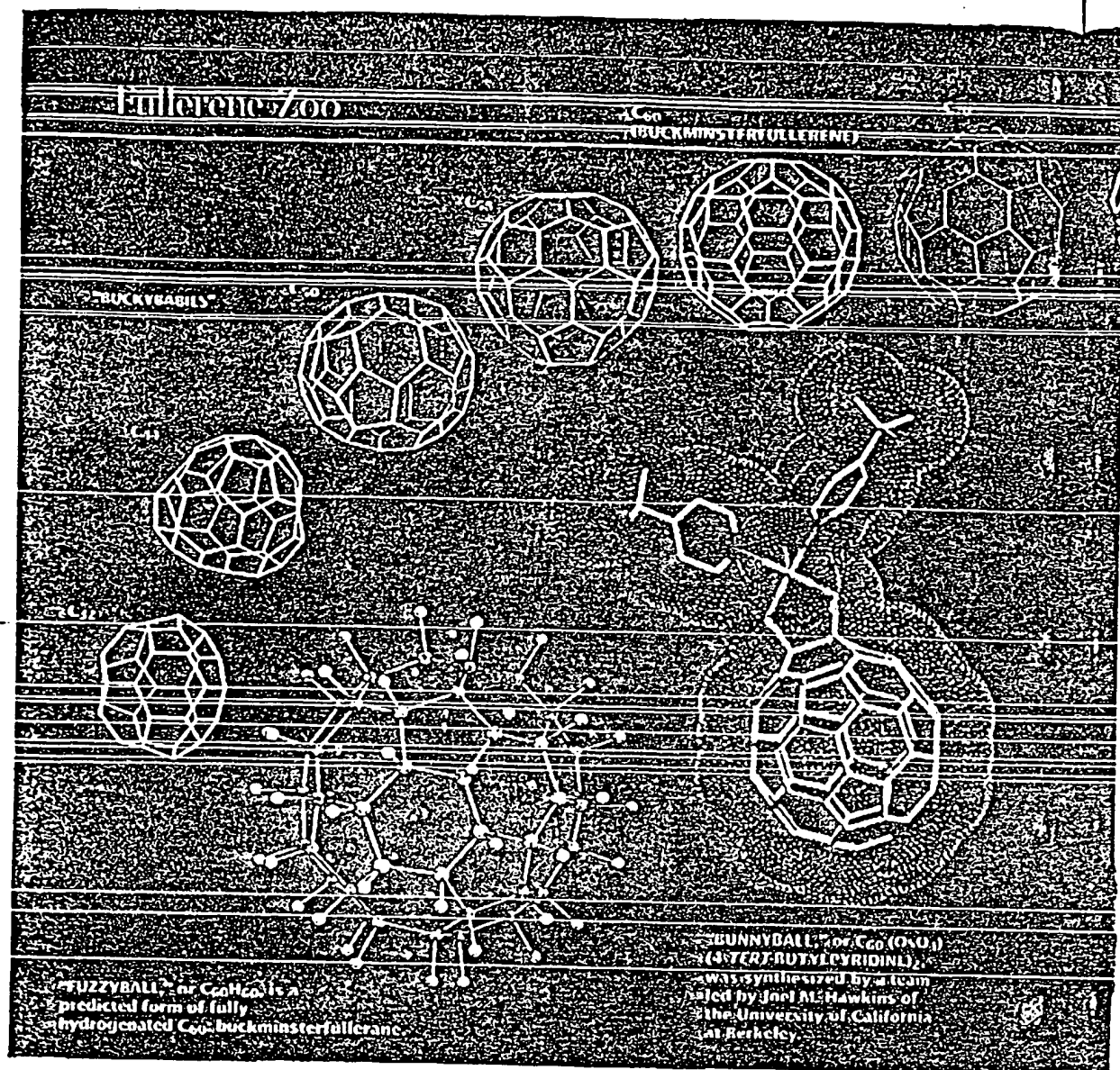
In the end, the breakthrough was made not by chemists but by physicists working in a totally different area. Huffman, Krätschmer and their students had been engaged for decades in a study of interstellar dust, which they assumed to consist mainly of particles of carbon (the most common particle-forming element). They therefore modeled the phenomenon in the laboratory by vaporizing carbon and condensing it in as many ways as possible. Optical tests figured in most of the studies. (Virtually all that is known of the interstellar dust stems from obser-

vations of how it absorbs and scatters starlight.)

In 1983 the physicists tried evaporating a graphite rod by resistive heating in an atmosphere of helium. They noticed that when the helium pressure was just right (about a seventh of an atmosphere), the dust strongly absorbed wavelengths in the far ultraviolet region, creating a peculiar, double-humped spectrum [see bottom illustration on page 58]. Most observers would have missed the two blips on the screen, but not Huffman and Krätschmer: they had studied spectra of carbon dust for years without encountering such an effect. They dubbed it their "camel" sample and wondered what it meant.

Nearly three years later, in the late fall of 1985, Huffman read in *Nature* of



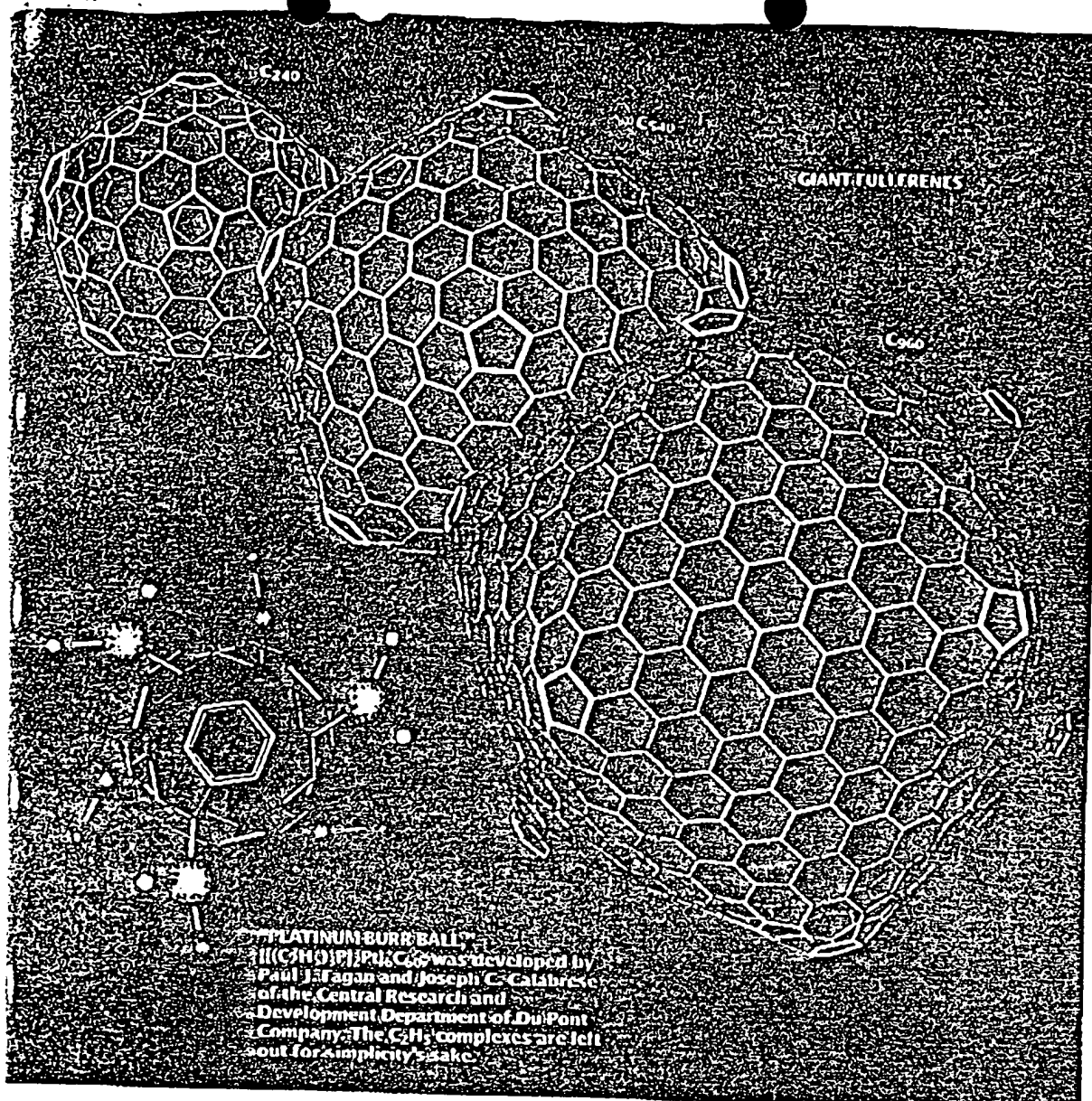


our discovery of C_{60} and began to wonder if a hollow soccerball molecule might be the cause of the double hump. Yet this explanation seemed too good to be true, for it required that C_{60} account for a significant portion of the sample. Why would so much of the carbon end up in such perfectly symmetric cages? What did the helium do to make it possible? The seeming unlikelihood of this hypothesis, together with some difficulty in reproducing the experiment, led the researchers to put the project on the back burner.

By 1989, however, Huffman and Krätschmer had become convinced that the C_{60} hypothesis ought to be reexamined. They renewed their interest in the camel sample, readily reproducing the results of the 1983 experiments. This time their attention turned to measuring the sample's absorption of infrared light—the wavelengths that interact with the vibrational motion of molecules—in order to test the results against theoretical predictions that had by now been made for soccerball C_{60} . These predictions held that of the 174

vibrational modes of this putative molecule, only 46 would be distinct, and only four would appear in the infrared range. To their surprise, they found the camel sample did display four sharp infrared absorption lines, and they verified that the lines were present only in carbon dust produced in the special camel way. This finding provided striking evidence that C_{60} might be present in abundance.

Influenced by their background in physics, the workers initially chose to test their hypothesis by a rather in-



involved route. They prepared a sample from pure ¹³C, a heavy isotope of carbon, and verified that the extra mass shifted the four infrared bands in the way expected for so large a molecule composed exclusively of carbon. Ultimately, however, they realized that the simplest assay followed a basic dictum of organic chemistry: like dissolves like. Should their sample dissolve in an aromatic solvent, such as benzene, this would support the predicted aromaticity of C₆₀. Because benzene molecules take the shape of a ring of carbon at-

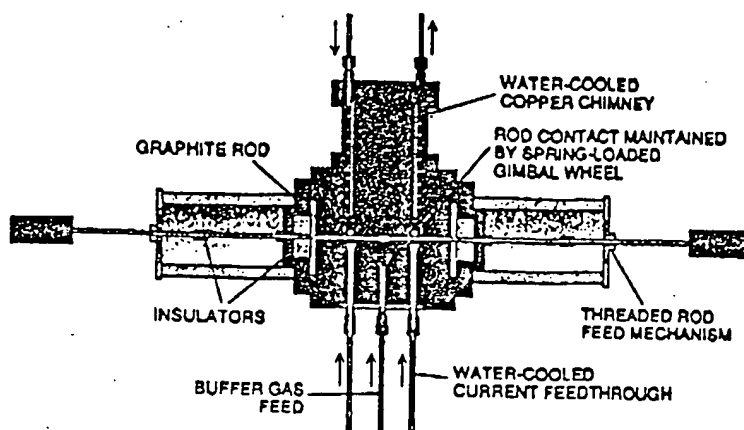
oms, C₆₀ would thus be seen as a kind of spherical benzene.

When the Krätschmer-Huffman group finally added benzene to their camel sample and saw the color red develop, they realized they were looking at the first concentrated solution of fullerenes ever seen. They evaporated the solvent and found that tiny crystals remained, which readily redissolved. These crystals could be sublimed under a vacuum near 400 degrees Celsius and condensed on a cold microscope slide to form smooth films of solid materials,

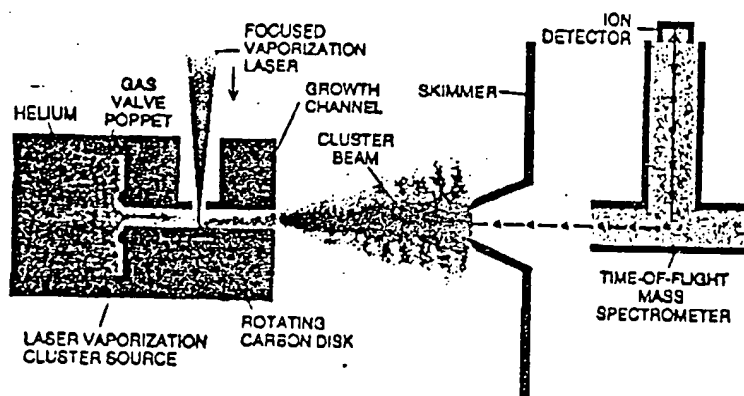
which Krätschmer and Huffman christened "fullerite."

In thin layers these films were yellow (a fact that those of us at Rice University who searched for a "yellow vial" find highly gratifying). Although it took a while to obtain precise numbers, it is now known that carbon dust prepared in the camel way produces an extractable fullerene mixture made up of roughly 75 percent C₆₀ (the soccer ball), 23 percent C₇₀ (the rugby ball) and a grab bag of larger fullerenes.

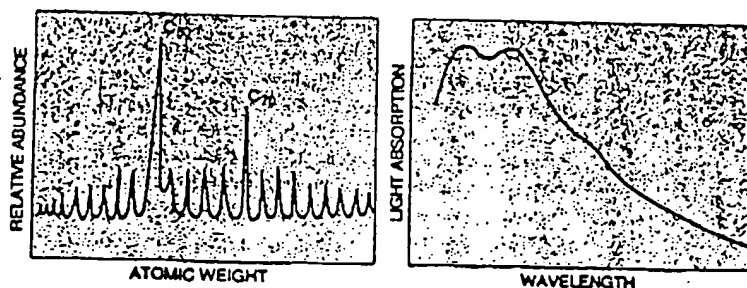
Here was a new form of pure, solid



FULLERENE FACTORY makes macroscopic samples in a carbon arc. The arc—a refinement of an apparatus developed by Wolfgang Krätschmer and Donald Huffman—frees carbon atoms that coalesce into sheets. Inert helium holds the sheets near the arc long enough for them to close in on themselves, forming fullerenes.



CLUSTER GENERATOR designed by one of the authors (Smalley) produced the first evidence that fullerenes can form from carbon vapor. A pulsed laser vaporizes carbon; a gust of helium then sweeps the vapor into a supersonic beam whose expansion cools the atoms, condensing them.



CRUCIAL GRAPHS: In 1985 the cluster-beam generator showed many even-numbered carbon clusters, especially C_{60} , suggesting that these species are particularly stable. The humped ultraviolet absorption spectrum led Krätschmer and Huffman to dub it the "camel" sample; in 1990 it was shown to contain C_{60} .

carbon. It is the only pure, finite form. The other two, diamond and graphite, are actually infinite network solids. In the real world, one usually deals with hunks of diamond cut out of larger bulk crystals. Under normal conditions, the surfaces of such a piece are instantly covered with hydrogen, which ties up the dangling surface bonds. Graphite is much the same. No piece of diamond, therefore, can ever be truly pure under normal conditions. The fullerenes, on the other hand, need no other atoms to satisfy their chemical bonding requirements on the surface. In this sense, the fullerenes are the first and only stable forms of pure, finite carbon.

Once the Krätschmer-Huffman results were announced at a conference in Konstanz, Germany, in early September 1990, the race was on. The study of C_{60} and the fullerenes had been the province of the few select groups that had something like our elaborate and expensive laser-vaporization cluster-beam apparatus. Now Krätschmer and Huffman had opened the field to anyone who could procure a thin rod of carbon, a cheap power supply, a bell-jar vacuum chamber and a few valves and gauges. Everybody could play.

Within a few months, many groups were making their own fullerenes. Physicists, chemists and materials scientists thus began an interdisciplinary feeding frenzy that continues to intensify as this article is being written (see box on page 62). The key results have been quickly reproduced in over a dozen laboratories, some of which have applied alternative procedures of verification as well. Because fullerenes are readily soluble and vaporizable molecules that remain stable in air, they are perfectly suited to a wide range of techniques.

One of the most powerful techniques—nuclear magnetic resonance (NMR)—has confirmed the single most critical aspect of the soccerball structure: that all 60 carbon atoms have exactly the same relation to the whole. Only the truncated icosahedral structure we proposed for C_{60} arranges the atoms so symmetrically as to distribute the strain of closure equally. Such even distribution makes for great strength and stability. Indeed, that is why we proposed the structure in the first place: It explains the extraordinary stability of the 60-atom species.

Because C_{60} is the most symmetric molecule possible in three-dimensional Euclidean space, it is literally the roundest of round molecules. Edgeless, chargeless and unbound, the molecule spins freely, as NMR experiments show.

more than 100 million times a second. The NMR experiments also dramatically verify that C_{60} has the shape of a tiny rugby ball: at room temperature, it spins rapidly about its long axis, stopping its frantic motion only below the temperature of liquid air.

High-resolution electron microscopy revealed these little carbon balls one at a time—as predicted, they spanned a bit more than one nanometer (a billionth of a meter). Scanning tunneling microscopy showed that when C_{60} molecules are deposited on a crystalline surface, they pack as regularly as billiard balls. X-ray diffraction studies demonstrated that—as one would expect— C_{60} crystallizes in a face-centered cubic lattice, with the balls a little more than 10 angstroms apart [see illustration on page 62]. The crystals are as soft as graphite. When squeezed to less than 70 percent of their initial volume, calculations predict that they will become even harder than diamond. When the pressure is relieved, they are observed to spring back to their normal volume. Thrown against steel surfaces at speeds somewhat greater than 17,000 miles per hour (about the orbital speed of the U.S. space shuttle), they are incredibly resilient: they just bounce back.

We found that the most convenient way to generate fullerenes consists of setting up an arc between two graphite electrodes. We maintained a constant gap by screwing the electrodes toward each other as fast as their tips evaporated. The process worked best when the helium pressure was optimized and other gases, such as hydrogen and water vapor, were rigorously eliminated. Such measures produced yields of dissolvable fullerenes that typically ranged between 10 and 20 percent of the vaporized carbon. Yields as high as 45 percent have recently been reported.

The only irreducible cost appears to be that of the electricity needed to run the arc. But even the small bench-top generators we are now using in our laboratory provide electricity at a cost that amounts to only about five cents per gram of C_{60} . Recently it has been found that a sooting flame (such as that of a candle) can be used to produce substantial yields of C_{60} . In the long run, this may prove the cheapest way to make the material. When the first large-scale applications of fullerenes are found—perhaps in superconductors, batteries or microelectronics [see box on page 62]—the manufacturing cost of C_{60} will probably fall close to that of aluminum: a few dollars a pound. What had recently been described as the "most controversial molecule in the

Cosmos" is well on its way to becoming a bulk commodity.

A host of questions arises out of this wonder. What exactly is the helium doing? How can such a perfectly symmetric molecule be formed with such high efficiency out of the chaos of a carbon arc? And, on a more personal level, where did we go wrong? Why did we, and all other chemists for that matter, fail in the search for the yellow vial? Our technique involved helium as well. What did the Krätschmer-Huffman team do that made such a big difference?

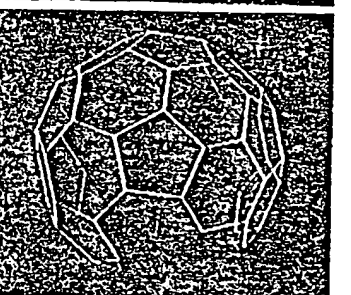
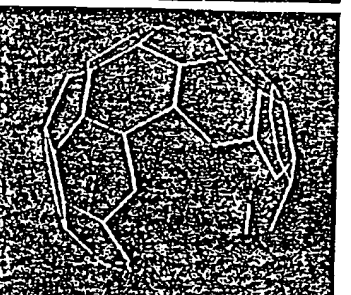
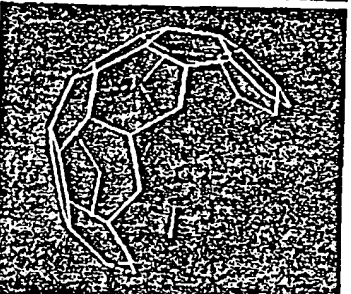
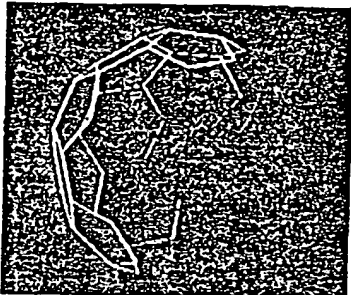
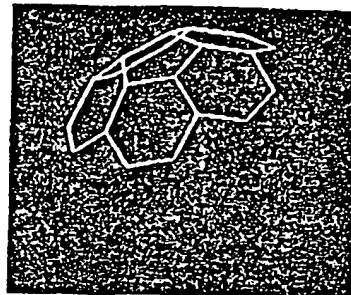
We now believe the answers to these questions lie in the way carbon vapor condenses at high temperatures. Linear carbon chains appear to link together to form graphitic sheets, and the sheets anneal as they grow in the hot vapor. Finally, stable, cage-like structures are favored by a key concept, which we call the pentagon rule.

Scientists had long known that when carbon is vaporized, most of its atoms initially coalesce into clusters ranging from two to 15 atoms or so. The very smallest carbon molecules are known to prefer essentially one-dimensional geometries. But clusters containing at least 10 atoms most commonly form a monocyclic ring—a kind of molecular Hula-Hoop that is especially favored at low temperatures. At very high temperatures, the rings break open to form units that comprise as many as 25 carbon atoms, taking the form of linear chains. Such chains might be imagined to look something like writhing snakes as they vibrate in the hot vapor.

It was these linear carbon chains that initially got us involved in carbon cluster studies and led to the discovery of C_{60} . Our British colleague, Harry Kroto, had theorized that the great abundance of such linear carbon chains in interstellar space may arise from chemical reactions in the outer atmospheres of carbon-rich red giant stars. In the early 1980s one of us (Smalley) had developed a supersonic cluster-beam device for the general study of small clusters composed of essentially any element in the periodic table [see "Microclusters," by Michael A. Duncan and Dennis H. Rouvray; *SCIENTIFIC AMERICAN*, December 1989].

We produced clusters by focusing an intense pulsed laser on a solid disk of the element to be studied. The local temperature could readily be brought above 10,000 degrees C—hotter than the surface of most stars and certainly hot enough to vaporize any known material. The resulting vapor was entrained in a powerful gust of helium, a chemi-

Growth of a Buckyball



cally inert carrier gas, which cooled the vapor so that it could condense into small clusters. As the carrier gas expanded through a nozzle into a vacuum, it generated a supersonic beam of clusters whose sizes could be measured by a mass spectrometer.

In 1984 a group at Exxon using a copy of the cluster-beam apparatus developed at Rice had been the first to study carbon clusters in this fashion. Their results strongly suggested that the linear carbon chains Kroto wanted to study were in fact being produced in abundance. In addition, they reported a bizarre pattern among the larger clusters: the distribution was strikingly lacking in the species having an odd number of atoms.

The Exxon researchers recorded but did not notice that two particular even-numbered members, C_{60} and C_{70} , were somewhat more abundant than their neighbors (see bottom illustration on page 58). The mysterious even-numbered distribution of clusters was separated from the small linear-chain distribution by what appeared to be something of a forbidden zone—a region of clusters between roughly 25 and 35 atoms in size in which few if any clusters could be detected.

The even-numbered distribution was soon discovered to result from the fullerenes. In one of our many studies of Kroto's linear carbon chains, we reproduced the Exxon results but found something quite striking about the distribution of large, even-numbered clusters. Heath, Kroto and O'Brien noticed that the 60th cluster seemed five times more abundant than any other even-numbered cluster in the range between 50 and 70 atoms. This differential was dramatically greater than anything that had been seen before.

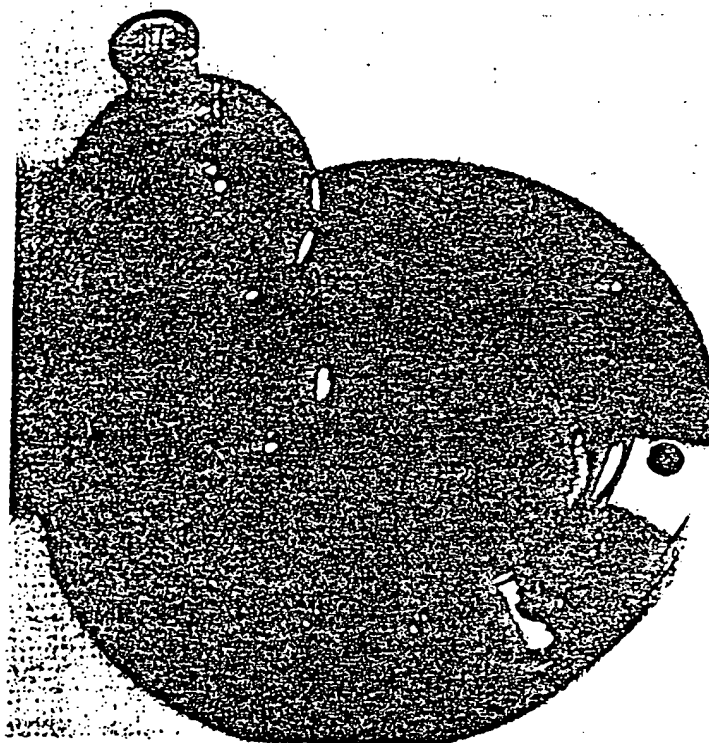
After much discussion, Heath and O'Brien spent the next weekend playing with the conditions in the laser-vaporization machine's supersonic nozzle. By Monday morning they had managed to find conditions in which C_{60} stood out in the cluster distribution like a flagpole. By the next morning we had had our Eureka! experience, and we were playing with every sort of soccerball we could get our hands on.

We found that we could explain the dominance of the even-numbered clusters by assuming they had all taken the structure of hollow, geodesic domes. They were all fullerenes. We could also argue that some fullerenes were more abundant than others because of the smoothness of the clusters' surface and the natural grouping of pentagons.

Pentagons provided an important clue. Although hundreds of examples are known in chemistry of five-membered rings attached to six-membered rings in stable aromatic compounds (for example, the nucleic acids adenine and guanine), only a few occur whose two five-membered rings share an edge. Interestingly, the smallest fullerene in which pentagons need not share an edge is C_{60} ; the next is C_{70} . Although C_{70} and all larger fullerenes can easily adopt structures in which the five-membered rings are well separated, one finds that these pentagons in the larger fullerenes occupy strained positions.

This vulnerability makes the carbon atoms at such sites particularly susceptible to chemical attack.

The big question, however, was not why fullerenes were stable but rather how they formed so readily in laser-vaporized graphite. Near the end of 1985, we suggested that the process began with linear chains. As the carbon vapor began to condense, the linear chains would grow long enough to flip back on themselves to form large monocyclic Hula-Hoops. As the growth continued, the chains would also fold into more effectively connected polycyclic network structures. Because graphite,



COLOR OF C_{60} depends on its form. This yellow film was sublimed onto a glass window that had been bolted to a vacuum oven. The benzene solution is magenta.



FULLERENE CRYSTALS were produced by evaporating a benzene solution of C_{60} containing a significant admixture of C_{70} .

the most stable known form of carbon, has its atoms bound in infinite hexagonal sheets, we suspected that the polycyclic network clusters resembled pieces of such sheets. We expected it to look like a fragment of chicken wire.

Like a cutout section of chicken wire,

these graphitic sheets would have many dangling bonds, making them chemically reactive—much more so than the smaller linear chains, which have only two such bonds, one on each end. The sheets, therefore, would not be expected to be abundant in the cluster beams.

Almost as soon as they form, they react with other small carbon molecules and grow too large to be seen. This, we believe, explains why there is a forbidden zone between the small linear-chain distribution and the first small fullerenes. Chemists are conditioned to think of

Fullerene Electronics

Currently the most technologically interesting properties of bulk C_{60} are electronic: In various compound forms it functions as an insulator, a conductor, a semiconductor and a superconductor.

The material crystallizes when C_{60} molecules pack together like Ping-Pong balls in a face-centered cubic lattice. Calculations over the past few months have predicted that this new material is a direct band-gap semiconductor like gallium arsenide. All its units stand precisely at their posts in a crystalline structure. But unlike the elements of gallium arsenide, the buckyballs spin freely and at random. This disorder gives them a certain resemblance to amorphous silicon—a constituent of inexpensive solar cells. The peculiar disorder within order of bulk C_{60} has yet to be fully explored, but it is expected to produce a wholly new kind of semiconductor.

Early in 1991 researchers at AT&T Bell Laboratories discovered that they could mix, or dope, C_{60} with potassium to produce a new metallic phase—a "buckide" salt. It reaches its maximum electrical conductivity when there are three potassium atoms to each buckyball. If too much potassium is added, however, the material becomes insulating. Subsequent work has shown that K_3C_{60} is a stable metallic crystal consisting of a face-centered cubic structure of buckyballs, with potassium ions filling the cavities between the balls. Potassium buckide is the first completely three-dimensional molecular metal.

The Bell Labs team further discovered that this K_3C_{60} metal becomes a superconductor when cooled below 18 kelvins. When rubidium is substituted for the potassium, the critical temperature for superconductivity was found to be near 30 kelvins. (Recently workers at Allied-Signal, Inc., detected superconductivity at 43 kelvins for rubidium-thallium-doped material.) Careful work at the University of California at Los Angeles has shown that the superconducting phase is stable and readily annealed—imperfections can be smoothed away by heating and cooling.

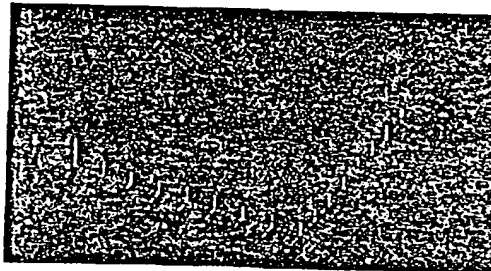
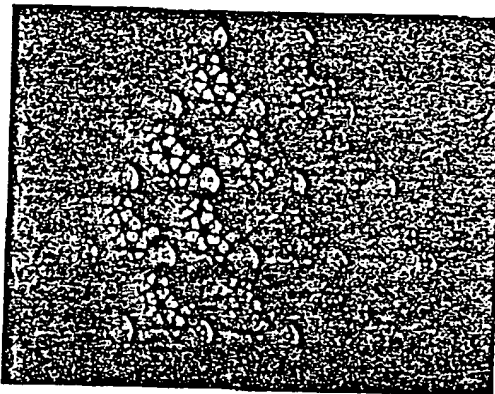
The material can therefore be manufactured as a three-dimensional superconductor, making it a candidate for practical superconducting wires. Early estimates of magnetic and other characteristics indicate that these superconducting buckide salts are similar to the high-temperature superconducting ceramics made of yttrium, barium and copper oxide.

Recent work at the University of Minnesota has shown that highly ordered C_{60} films can readily be grown on crystalline substrates, such as gallium arsenide. This attribute makes the film a suitable material for microelectronic fabrication. Beautifully regular films of the K_3C_{60} superconductor can also be made (see micrograph at right), and the interface between the C_{60} crystalline film and the K_3C_{60} material has been found to be stable. It may thus lend itself to the production of intricately layered microelectronic devices.

In order for the semiconducting properties of fullerene materials to be thoroughly exploited, scientists need to

learn how to dope them selectively to make *n*-type and *p*-type fullerene films, which donate electrons and holes, respectively. Such doping may involve putting a dopant atom inside the cage, either by growing the cage around the atom or by shooting atoms through the carbon walls by brute force. Small atoms, such as helium, have already been injected this way into the C_{60} cage, and it seems likely that hydrogen and lithium are insertable as well.

The versatility of bulk C_{60} seems to grow week by week. As we go to press, for example, there is a report suggesting that fullerene complexes exhibit ferromagnetic qualities in the absence of metals, an unparalleled phenomenon. Also, British workers from the universities of Leicester, Southampton and Sussex have just reported the generation of macroscopic quantities of fully fluorinated buckyballs ($C_{60}F_{60}$). The resulting "teflon balls" may be among the world's best lubricants. We do not know what the fullerenes' burgeoning traits will allow, but it would be surprising if the possibilities are not wonderful.



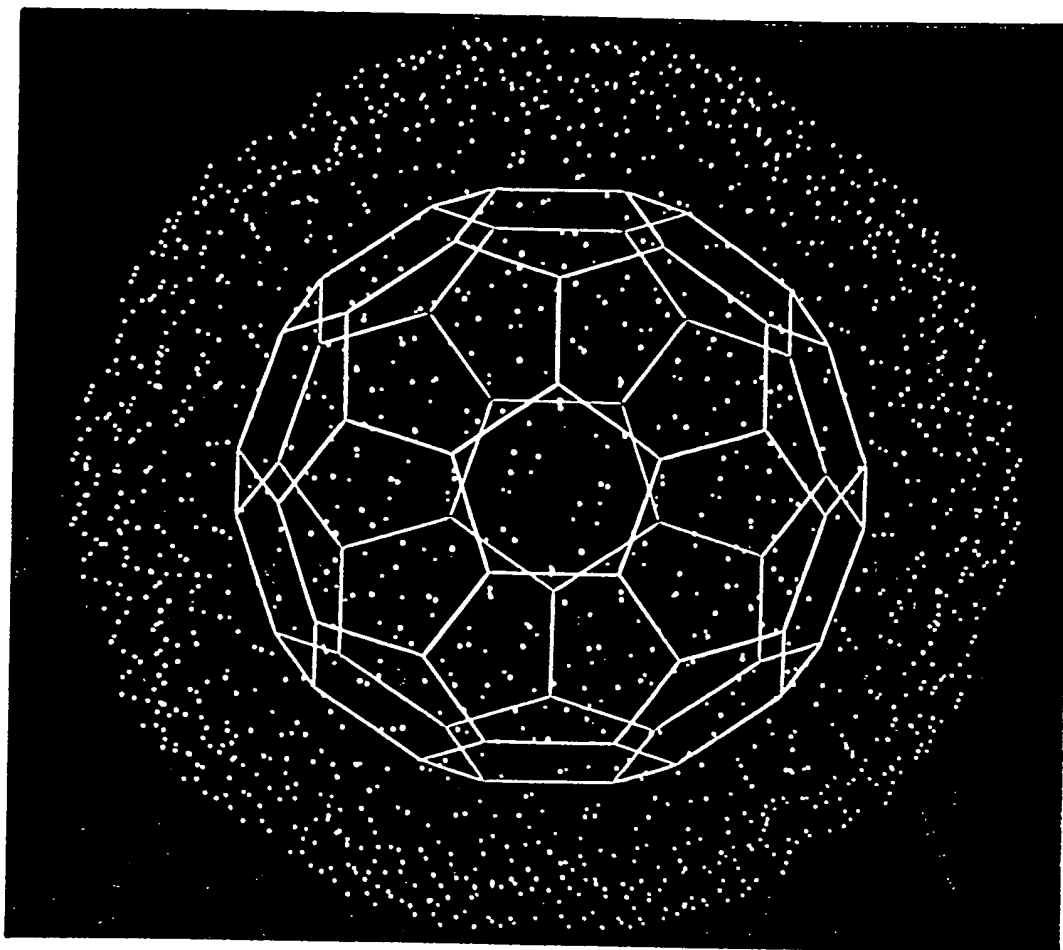
SUPERCONDUCTING FULLERIDE forms when buckyballs are doped with potassium in the ratio of K_3C_{60} (diagram), producing a crystal that can be grown on a gallium arsenide substrate (scanning tunneling micrograph).

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SIXTY-CARBON CLUSTER

AUTUMN BOOKS

Harvey Brooks
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P. N. Johnson-Laird
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(steps through the cosmos)

C₆₀: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl
& R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical
Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells¹, graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C₆₀ molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

The technique used to produce and detect this unusual molecule involves the vaporization of carbon species from the surface of a solid disk of graphite into a high-density helium flow, using a focused pulsed laser. The vaporization laser was the second harmonic of Q-switched Nd:YAG producing pulse energies of ~30 mJ. The resulting carbon clusters were expanded in a supersonic molecular beam, photoionized using an excimer laser, and detected by time-of-flight mass spectrometry. The vaporization chamber is shown in Fig. 2. In the experiment the pulsed valve was opened first and then the vaporization laser was fired after a precisely controlled delay. Carbon species were vaporized into the helium stream, cooled and partially equilibrated in the expansion, and travelled in the resulting molecular beam to the ionization region. The clusters were ionized by direct one-photon excitation with a carefully synchronized excimer laser pulse. The apparatus has been fully described previously²⁻⁵.

The vaporization of carbon has been studied previously in a very similar apparatus⁶. In that work clusters of up to 190 carbon atoms were observed and it was noted that for clusters of more than 40 atoms, only those containing an even number of atoms were observed. In the mass spectra displayed in ref. 6, the C₆₀ peak is the largest for cluster sizes of >40 atoms, but it is not completely dominant. We have recently re-examined this system and found that under certain clustering conditions the C₆₀ peak can be made about 40 times larger than neighbouring clusters.

Figure 3 shows a series of cluster distributions resulting from variations in the vaporization conditions evolving from a cluster distribution similar to that observed in ref. 3, to one in which C₆₀ is totally dominant. In Fig. 3c, where the firing of the vaporization laser was delayed until most of the He pulse had passed, a roughly gaussian distribution of large, even-numbered clusters with 38-120 atoms resulted. The C₆₀ peak was largest but not dominant. In Fig. 3b, the vaporization laser was fired at the time of maximum helium density; the C₆₀ peak grew into a feature perhaps five times stronger than its neighbours, with the exception of C₇₀. In Fig. 3a, the conditions were similar to those in Fig. 3b but in addition the integrating cup depicted in Fig. 2 was added to increase the time between vaporization and expansion. The resulting cluster distribution is completely dominated by C₆₀; in fact more than 50% of the total large cluster abundance is accounted for by C₆₀; the C₇₀ peak has diminished in relative intensity compared with C₆₀, but remains rather prominent, accounting for ~5% of the large cluster population.

Our rationalization of these results is that in the laser vaporization, fragments are torn from the surface as pieces of the planar

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C₆₀ molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.



graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise from a graphite fragmentation, this result seems impossible: there is not much to choose between such isomers in terms of stability. If one tries to shift to a tetrahedral diamond structure, the entire surface of the cluster will be covered with unsatisfied valences. Thus a search was made for some other plausible structure which would satisfy all sp² valences. Only a spheroidal structure appears likely to satisfy this criterion, and thus Buckminster Fuller's studies were consulted (see, for example, ref. 7). An unusually beautiful (and probably unique) choice is the truncated icosahedron depicted in Fig. 1. As mentioned above, all valences are satisfied with this structure, and the molecule appears to be aromatic. The structure has the symmetry of the icosahedral group. The inner and outer surfaces are covered with a sea of π electrons. The diameter of this C₆₀ molecule is ~7 Å, providing an inner cavity which appears to be capable of holding a variety of atoms⁸.

Assuming that our somewhat speculative structure is correct, there are a number of important ramifications arising from the existence of such a species. Because of its stability when formed under the most violent conditions, it may be widely distributed in the Universe. For example, it may be a major constituent of circumstellar shells with high carbon content. It is a feasible constituent of interstellar dust and a possible major site for

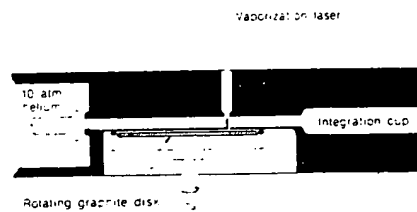


Fig. 2 Schematic diagram of the pulsed supersonic nozzle used to generate carbon cluster beams. The integrating cup can be removed at the indicated line. The vaporization laser beam (30-40 mJ at 532 nm in a 5-ns pulse) is focused through the nozzle, striking a graphite disk which is rotated slowly to produce a smooth vaporization surface. The pulsed nozzle passes high-density helium over this vaporization zone. This helium carrier gas provides the thermalizing collisions necessary to cool, react and cluster the species in the vaporized graphite plasma, and the wind necessary to carry the cluster products through the remainder of the nozzle. Free expansion of this cluster-laden gas at the end of the nozzle forms a supersonic beam which is probed 1.3 m downstream with a time-of-flight mass spectrometer.

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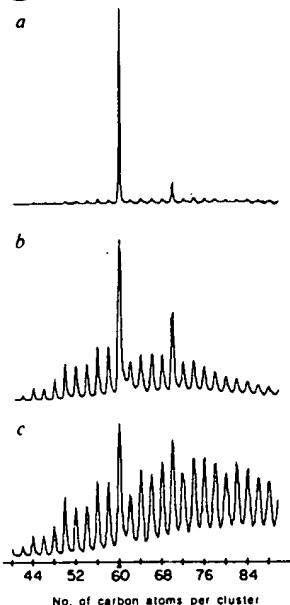


Fig. 3 Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV , 1 mJ cm^{-2}). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In *c*, the effective helium density over the graphite target was less than 10 torr—the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in *b* was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. The enhancement of C_{60} and C_{70} is believed to be due to gas-phase reactions at these higher clustering conditions. The spectrum in *a* was obtained by maximizing these cluster thermalization and cluster-cluster reactions in the 'integration cup' shown in Fig. 2. The concentration of cluster species in the especially stable C_{60} form is the prime experimental observation of this study.

surface-catalysed chemical processes which lead to the formation of interstellar molecules. Even more speculatively, C_{60} or a derivative might be the carrier of the diffuse interstellar lines⁹.

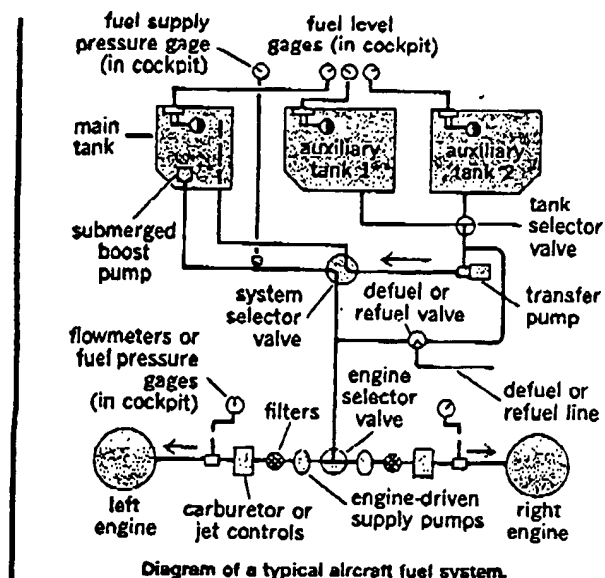
If a large-scale synthetic route to this C_{60} species can be found, the chemical and practical value of the substance may prove extremely high. One can readily conceive of C_{60} derivatives of many kinds—such as C_{60} transition metal compounds, for example, C_{60}Fe or halogenated species like $\text{C}_{60}\text{F}_{60}$ which might be a super-lubricant. We also have evidence that an atom (such as lanthanum⁸ and oxygen¹) can be placed in the interior, producing molecules which may exhibit unusual properties. For example, the chemical shift in the NMR of the central atom should be remarkable because of the ring currents. If stable in macroscopic, condensed phases, this C_{60} species would provide a topologically novel aromatic nucleus for new branches of organic and inorganic chemistry. Finally, this especially stable and symmetrical carbon structure provides a possible catalyst and/or intermediate to be considered in modelling prebiotic chemistry.

We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this C_{60} species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for example, ballene, sphere, soccerene, carbosoccer), but we prefer to let this issue of nomenclature be settled by consensus.

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is usually such that all the fuel supply will pass to the engines by way of the main tank, which is refilled as necessary from the auxiliary tanks. In case of emergency, the system selector valve may connect the auxiliary tanks to the engines directly. [F.C.M./J.A.B.]

Fugacity A function introduced by G. N. Lewis to facilitate the application of thermodynamics to real systems. Thus, when fugacities are substituted for partial pressures in the mass action equilibrium constant expression, which applies strictly only to the ideal case, a true equilibrium constant results for real systems as well.

The fugacity f_i of a constituent i of a thermodynamic system is defined by the following equation (where μ_i is the chemical

$$\mu_i = \mu_i^* + RT \ln f_i$$

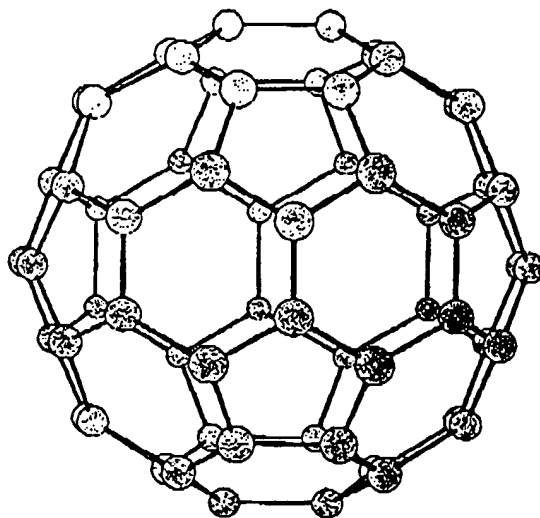
potential and μ_i^* is a function of temperature only), in combination with the requirement that the fugacity approach the partial pressure as the total pressure of the gas phase approaches zero. At a given temperature, this is possible only for a particular value for μ_i^* , which may be shown to correspond to the chemical potential the constituent would have as the pure gas in the ideal gas state at 1 atm pressure. This definition makes the fugacity identical to the partial pressure in the ideal gas case. For real gases, the ratio of fugacity to partial pressure, called the fugacity coefficient, will be close to unity for moderate temperatures and pressures. At low temperatures and appropriate pressures, it may be as small as 0.2 or less, whereas at high pressures at any temperature it can become very large. See ACTIVITY (THERMODYNAMICS); CHEMICAL EQUILIBRIUM; CHEMICAL THERMODYNAMICS; GAS. [P.J.B.]

Fullerene A molecule containing an even number of carbon atoms arranged in a closed hollow cage. The fullerenes were discovered as a consequence of astrophysically motivated chemical physics experiments that were interpreted by using geodesic architectural concepts. Fullerene chemistry, a new field that appears to hold much promise for materials development and other applied areas, was born from pure fundamental science. See CARBON.

In 1985, fifteen years after it was conceived theoretically, the molecule buckminsterfullerene (C_{60} or fullerene-60) was discovered serendipitously. Fullerene-60 (see illustration) is the archetypal member of the fullerenes, a set of hollow, closed-cage molecules consisting purely of carbon. The fullerenes can be considered, after graphite and diamond, to be the third well-defined allotrope of carbon.

In the fullerene molecule an even number of carbon atoms are arrayed over the surface of a closed hollow cage. Each atom is trigonally linked to its three near neighbors by bonds that delineate a polyhedral network, consisting of 12 pentagons and n hexagons. All 60 atoms in fullerene-60 are equivalent and lie on the surface of a sphere distributed with the symmetry of a truncated icosahedron. The 12 pentagons are isolated and interspersed symmetrically among 20 linked hexagons; that is, the symmetry is that of a modern soccerball. The molecule was named after R. Buckminster Fuller, the inventor of geodesic domes, which conform to the same underlying structural formula. Three of the four valence electrons of each carbon atom are involved in the sp^2 sigma-bonding skeleton, and the fourth p electron is one of 60 involved in a π -delocalized molecular-orbital electron sea that covers the outside (exo) and inside (endo) surface of the molecule. The resulting cloud of π electron density is similar to that which covers the surface of graphite; indeed, the molecule can be considered a round form of graphite. See ELECTRON CONFIGURATION; GRAPHITE.

Fullerene-60 behaves as a soft electrophile, a molecule that readily accepts electrons during a primary reaction step. It can accept three electrons readily and perhaps even more. The molecule can be multiply hydrogenated, methylated, ammoniated, and fluorinated. It forms exohedral complexes in which an atom (or group) is attached to the outside of the cage, as well as endohedral complexes in which an atom (for example, lanthanum (La), potassium (K), or calcium (Ca)) is trapped inside the cage.



Structure of C_{60} (buckminsterfullerene).

Fullerene materials have been available for such a short time that applications are yet to be established. However, the properties already discovered suggest that there is likely to be a wide range of areas in which the fullerenes or their derivatives will have uses.

Fullerene-60 was discovered as a direct result of physico-chemical investigations that simulated processes occurring in stars and in space. Consequently the likelihood that fullerenes, in particular fullerene-60, and analogs are present in space is a fascinating conjecture. [H.W.J.]

Fuller's earth Any natural earthy material (such as clay materials) which decolorizes mineral or vegetable oils to a sufficient extent to be of economic importance. It has no mineralogic significance. The clay minerals present in fuller's earth may include montmorillonite, attapulgite, and kaolinite.



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